THE SEPARATION OF PHENOLIC COMPOUNDS FROM NEUTRAL OILS AND NITROGEN BASES

by

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DECLARATION

I, the undersigned, hereby declare that this dissertation is my own original work, except where specifically acknowledged in the text. Neither the present dissertation, nor any part thereof, has previously been submitted for a degree at any university.

Denise Louisette Venter 12 February 2001

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SYNOPSIS

Coal pyrolysis liquors are a major source of phenolic compounds. The separation of the phenolic compounds from the neutral oils and nitrogen bases also present in the pyrolysis liquors is difficult due to low relative volatilities and the formation of azeotropes. The desired phenolic recovery and phenolic product purity of 99.5 % can therefore not be achieved by means of conventional separation processes.

Alternative processes such as liquid-liquid extraction with various low-boiling solvents, mixtures of high-boiling solvents and extractive distillation have been investigated. Disadvantages of these processes include the high solvent ratios required, low recovery of the higher substituted phenolic compounds, inability to treat a wide-boiling feedstock in one process step and complex post-purification of the phenolic product. A solvent system consisting of a selective solvent, water as a co-solvent, and hexane as a countersolvent, is proposed.

An industrial heavy naphtha stream was analysed and the most prevalent phenolic compounds, neutral oils and nitrogen bases identified. Three synthetic feed streams were compiled to represent the industrial stream, namely:

1. phenol + benzonitrile + aniline + mesitylene + 5-et-2-me-pyridine
2. m-cresol + o-tolunitrile + o-toluidine + pseudocumene + undecane + indene
3. 2,4-xylenol + 3,5-xylenol + 3,4-xylenol + indane + dodecane + naphthalene

The stream containing phenol was used as a basis for solvent selection, with emphasis on the separation of phenol from benzonitrile. A variety of molecules containing hydroxyl and ether functional groups were identified as potential solvents by means of computer-aided molecular design using a genetic algorithm. Of the commercially available solvents tested on batch extraction scale, triethylene glycol achieved the highest phenol-benzonitrile, phenol-aniline and phenol-5-et-2-me-pyridine separation factors as well as the highest phenol recovery.

It was concluded from the solvent selection process that effective solvents for the problem under investigation were those containing hydroxyl groups positioned on the molecule backbone in such a way as to facilitate hydrogen bonding with more than one phenolic molecule at a time. Two commercially unavailable solvents, 1,3-(ethoxy-2-hydroxy)-propane-2-ol and 1,3-(diethoxy-4-hydroxy)-propane-2-ol were therefore synthesised from ethylene glycol and diethylene glycol respectively. The molecular structures of these two solvents are analogous to that of triethylene glycol, and contain an additional hydroxyl group. The performance of the synthesised solvents was evaluated and compared to that of triethylene glycol on the basis of m-cresol-o-tolunitrile, 2,4-xylenol - o-tolunitrile, and 2,4-xylenol - o-toluidine separation factors and

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phenolic recoveries achieved by means of batch extraction tests. 1,3-(Diethoxy-4-hydroxy)-propane-2-ol yielded higher phenolic recoveries, but lower separation factors than did triethylene glycol. Triethylene glycol was therefore selected for further process development as it is commercially available.

A series of batch extractions were carried out on each of the synthetic feed streams using the proposed solvent system. For phenol and m-cresol, recoveries in excess of 99% were obtained in a single stage. Recoveries in excess of 98% were obtained for the xylenol isomers. It was found that the recoveries of the xylenol isomers were more sensitive to changes in the solvent ratios.

The separation of phenolic compounds from paraffins, naphthalene, indene, indane and the alkyl-substituted benzenes was trivial using the proposed solvent system. Highly satisfactory separation of the phenolic compounds from pyridines and aromatic nitriles was achieved. The separation of phenol from aniline, although satisfactory, was not as good.

The optimum solvent to feed, water to solvent and hexane to feed ratios were identified as being 3.0, 5.0 and 0.25 respectively.

Binary interaction parameters for the NRTL equation were obtained by regression of the equilibrium data from the batch extraction tests. The NRTL model fitted the equilibrium data satisfactorily.

The proposed solvent system was tested on pilot plant scale. The performance of the extraction column was optimised using a synthetic feed stream consisting of m-cresol, p-cresol, aniline and o-tolunitrile. The optimum solvent ratios and operating parameters were then implemented in further tests on an industrial heavy naphtha stream. A phenolic product purity of 99.75% was achieved for this stream. The corresponding phenolic recovery was in excess of 91 %.

The proposed separation process, including solvent recovery was simulated using the NRTL model with the experimentally determined interaction parameters. A single stream consisting of all the components used in the batch extraction tests was specified as the feed stream to the simulated process. A final simulated phenolic product purity of 99.5% and recovery in excess of 94% was obtained after solvent recovery. The optimum solvent to feed, hexane to feed and water to solvent ratios were determined as being 3.0, 5.0 and 0.25 in both the pilot plant tests and the simulated extraction process.

It can be concluded that the proposed separation process is successful in recovering high purity phenolic compounds from tar liquors. Further development of the process has commenced in industry.

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OPSOMMING

Die pirolise van steenkool is 'n belangrike bron van fenoliese verbindings. Die skeiding van die fenoliese komponente vanuit die neutrale olies ook teenwoordig in die pirolise mengsel word bemoeilik deur lae relatiewe vlugtighede en die vorming van aseotrope. Dit is dus nie moontlik om die gewenste hoë fenoliese herwinning en fenoliese produk suiwerheid van 99.5% d.m.v. konvensionele distilleerprosesse te behaal nie.

Alternatiewe prosesse soos ekstraktiewe distillasie en vloeistof-vloeistof ekstraksie met verskeie laagkokende oplosmiddels en mengsels van hoogkokende oplosmiddels is al ondersoek. Die hoë oplosmiddel verhoudings wat benodig word, lae herwinning van die hoërgesubstitueerde fenoliese verbindings, onvermoë om in een prosesstap 'n prosesstroom met 'n wye kookgebied te behandel en die ingewikkelde suiwering van die fenoliese produk tel onder die nadele van hierdie prosesse. 'n Oplosmiddelsisteem wat 'n selektiewe oplosmiddel, water as polêre oplosmiddel en heksaan as teenoplosmiddel bevat is as 'n alternatiewe proses voorgestel.

'n Industriële swaar nafta prosesstroom is ge-analiseer en die fenoliese verbindings, neutrale olies en stikstofbasisse met die hoogste konsentrasies daarin geïdentifiseer. Drie sintetiese strome is op grond van hierdie analise saamgestel om die industriële stroom te verteenwoordig:

1. fenol + benzonitriel + anilien + mesitileen + 5-et-2-me-piridien
2. m-kresol + o-tolunitriel +o-toluïdien + pseudokumeen + undekaan + indeen
3. 2,4-xilenol + 3,5-xilenol + 3,4-xilenol + indaan + dodekaan + naftaleen

Die fenolbevattende stroom is as basis vir oplosmiddelkeuring gebruik, met die klem op die skeiding van fenol vanuit benzonitriel. Verskeie molekules wat hidroksie- en eter funksionele groepe bevat is as potensiële oplosmiddels uitgeken d.m.v. rekenaar-gesteunde molekulêre ontwerp met 'n genetiese algoritme. Hierdie oplosmiddels is d.m.v. enkellading ekstraksie toetse geëvalueer. Die kommersieel beskikbare oplosmiddel wat die hoogste fenol-benzonitriel, fenol-anilien en fenol-5-et-2-me-piridien skeidingsfaktore, sowel as die hoogste fenol herwinning op enkellading ekstraksie toetsvlak gelewer het, was triëtileenglikol.

Vanuit die proses vir die keuse van 'n oplosmiddel was dit duidelik dat, vir hierdie skeidingsprobleem, die mees effektiewe oplosmiddels dié is met hidroksiel groepe wat so geposisioneer is in die oplosmiddel molekuul dat dit waterstofbindings kan vorm met meer as een fenoliese molekuul. Twee oplosmiddels wat nie kommersiëel beskikbaar is nie, 1,3-(etoksie-2-hidroksie)-propaan-2-ol en 1,3-(diëtoksie-4-hidroksie)-propaan-2-ol, is gesintetiseer vanuit etileenglikol en diëtileenglikol onderskeidelik. Die molekulêre strukture van hierdie twee oplosmiddels is analoog aan dié van triëtileenglikol en bevat

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'n addisionele hidroksielgroep. Die effektiwiteit van die gesintetiseerde oplosmiddels is geëvalueer en met dié van triëtileenglikol vergelyk op grond van m-kresol-o-tolunitriel, 2,4-xilenol - o-tolunitriel en 2,4-xilenol - o-toluïdien skeidingsfaktore en fenoliese herwinning behaal d.m.v. enkellading ekstraksie toetse. Hoër fenoliese herwinning en laer skeidingsfaktore is behaal met 1,3-(diëtoksie-4-hidroksie)-propaan-2-ol as met triëtileenglikol. Triëtileenglikol is dus gekies vir verdere prosesontwikkeling aangesien dit kommersiëel beskikbaar is.

Enkellading ekstraksie toetse is op elk van die sintetiese voerstrome uitgevoer met die voorgestelde oplosmiddelsisteem. Fenol- en m-kresol herwinning van meer as 99% en xilenol herwinning van meer as 98% is behaal. Die skeiding van fenoliese verbindings vanuit paraffiene, naftaleen, indeen, indaan en die alkielgesubstitueerde benseenverbindings is triviaal met die voorgestelde oplosmiddelsisteem. Hoogs aanvaarbare skeiding van fenoliese verbindings van die piridiene en aromatiese nitriele is vermag. Die skeiding van fenol en anilien is nie so goed nie, maar is nog steeds aanvaarbaar.

Die optimum oplosmiddel tot voer, water tot oplosmiddel en heksaan tot voer is as 3.0, 5.0 en 0.25 vasgestel.

Binêre interaksie parameters vir die NRTL vergelyking is verkry d.m.v. regressie van die ewewigsdata wat deur die enkelladingstoetse gegenereer is. Die NRTL model het die ewewigsdata goed gepas.

Die voorgestelde oplosmiddelsisteem is op loodsaanlegvlak getoets. Die werking van die ekstraksie kolom is ge-optimeer met 'n sintetiese voerstroom wat uit m-kresol, p-kresol, anilien en o-tolunitriel bestaan. Die optimum oplosmiddel verhoudings en bedryfstoestande is verder toegepas op 'n industriële swaar naftastroom. 'n Fenoliese suiwerheid van 99.75% is behaal met hierdie stroom. Die ooreenkomstige fenoliese herwinning was groter as 91%.

Die voorgestelde skeidingsproses, insluitende oplosmiddelherwinning is gesimuleer met die NRTL model wat op die eksperimentele data gepas is. 'n Enkele stroom wat bestaan het uit al die komponente wat in die enkelladingstoetse gebruik is, is as die voerstroom tot die gesimuleerde proses gespesifiseer. 'n Finale gesimuleerde fenoliese produksuiwerheid van 99.5% en herwinning groter as 94% is na oplosmiddelherwinning behaal. Die optimum oplosmiddel tot voer, heksaan tot voer en water tot oplosmiddel verhoudings is vasgestel as 3.0, 5.0 en 0.25 onderskeidelik vir beide die gesimuleerde proses en die loodsaanleg toetse.

Die voorgestelde skeidingsproses kan dus 'n hoogs suiwer fenoliese produk uit pirolisestrome herwin. Verdere ontwikkeling van die proses is in die industrie begin.

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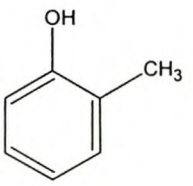
CHAPTER 1. INTRODUCTION

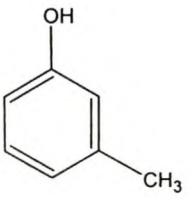
1.1 Phenolic Compounds

Each day tons of valuable building blocks for products as diverse as wire enamels, herbicides, explosives and perfume fixatives are discarded as low value coal tars. These versatile building blocks are the phenolic compounds, which are present in significant amounts in coal liquors.

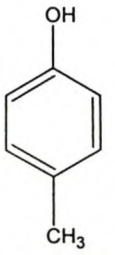
Phenolic compounds are alkyl derivatives of phenol. Apart from phenol itself, these include the three methylphenol, or cresol, isomers (C_7H_8O), six dimethylphenol, or xylenol, isomers ($C_8H_{10}O$) as well as higher substituted phenols such as ethyl phenols and C_3- and C_4- substituted phenols.



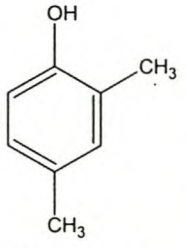
2-methylphenol
(o-cresol)



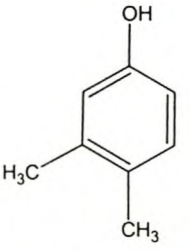
3-methylphenol
(m-cresol)



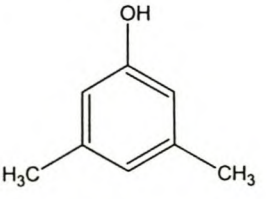
4-methylphenol
(p-cresol)



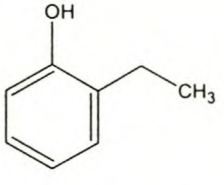
3,5-dimethylphenol
(3,5-Xylenol)



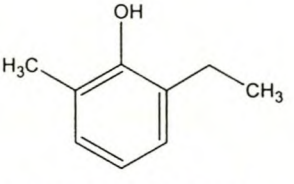
3,4-dimethylphenol
(3,4-Xylenol)



3,5-dimethylphenol
(3,5-Xylenol)



2-ethylphenol



2-ethyl-5-methylphenol

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1.2 Commercial Importance and Application

The phenolic products which are commercially significant are: 99+% phenol, 99+% o-cresol, 85+% m/p-cresol, mixed xylenols, mixed ethyl phenols and xylenols, alkyl phenols (C_3- and C_4-) and various blended phenolic mixtures [1].

o-Cresol is produced with a purity of 99.2-99.9 % for epoxy-o-cresol novolak (ECN) resins. Commonly used technical grades have purity levels of 98.2%-99%, ~96% and ~94%, in correspondence with grades A, B and C of the British Standard. m-Cresol is sold at purities of 99%, 98% and 96.5%. p-Cresol usually has a purity of 99%. Grades of ~95% and ~65% are also available where the main impurity is m-cresol [2].

Phenolic products with purities greater than 99.5% are commercially most desirable. Maximum concentrations of impurities commonly present in commercially available cresols are 0.2% water, 0.15% pyridine bases, 0.1% neutral oils and 0,01% sulphur [2].

Phenol recovered from coal tars competes directly with synthetic phenol. The natural phenol is a small portion of the total phenol market and is comparatively priced with synthetic phenol. The prices of phenol derivatives are influenced by the market price of phenol, benzene and toluene. Certain high purity isomers have values two to three times that of phenol due to complexity of synthesis and / or the complexity of the separation processes applied to recover them from natural sources [3]. Typical industrial prices are given for June 2000 in Table 1-1.

Table 1-1. Spot quotations and / or supplier list prices for phenolic compounds and related chemicals and materials for the week ending June 23, 2000 [4].

Chemical / Related Material	Purity / Description	Price
Coal Tar Pitch	Industrial Liquid Works	$ 3.10 / kg
Creosote	Coal Tar, f.o.b.	$ 0.11 / L
Naphtha	Petroleum tanks, f.o.b.	$ 0.21 - 0.23 / L
Phenol	Synthetic, f.o.b.	$ 0.84 / kg
m-Cresol	95-98% drums, f.o.b.	$ 2.76 / kg
m/p-Cresol	99% drums, f.o.b.	$ 2.25-2.31 / kg
m/p-Cresol	99% bulk, f.o.b.	$ 1.98 / kg
o-Cresol	99% drums / bulk f.o.b.	$ 1.62 / kg
p-Cresol	98% drums, f.o.b.	$ 4.14 / kg
p-Cresol	98% bulk, f.o.b.	$ 4.01 / kg
Xylenol	Drums	$ 12.35 / kg
Cresylic Acid	Coal Tar, m/p-cresol content >25%	$ 1.21 - 1.32 / kg
Benzene	Industrial	$ 0.18 / L
Toluene	Petroleum, f.o.b.	$ 2.71 / kg

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Most of the phenol produced is used for the production of phenol-formaldehyde resins and Bisphenol A which is becoming increasingly important as the starting material for polycarbonate and epoxy resins [3], [5]. Phenol is also used in the production of nylon, by a series of reactions which include the hydrogenation of the benzene ring, and in the production of plywood adhesives, binding material for fiberglass insulation and moulded electical components [5]. Phenol is also directly used in the production of aniline, adipic acid, salicylic acid, chlorophenols and alkylphenols [3].

An important field of application for technical grade cresol mixtures is the production of modified phenolic resins by condensation with formaldehyde. The suitability and price of cresol mixtures for this purpose depends on their content of m-cresol, the most reactive of the three isomers. Cresol mixtures are also very important solvents for synthetic resin coatings (wire enamels) [1].

o-Cresol is widely used in dye carriers, in the formulation of additives for lubricants and as an intermediate in herbicides, such as 2-methyl-4-chlorophenoxyacetic acid (MCPA), which are widely used in Europe and, increasingly, the United States. A small proportion of o-cresol is nitrated to form 4,6-dinitro-o-cresol, which has insecticidal as well as herbicidal properties [1]. Highly pure o-cresol is increasingly processed, especially in Japan, to ECN resins, which are used as sealing materials for integrated circuits. In addition, o-cresol is used in the production of antiseptics, fragrances and various antioxidants [2].

m-Cresol, either pure or in a mixture with p-cresol, is a starting material for contact insecticides such as Baytex. Pure m-cresol is also of considerable importance in the production of fragrance and flavour substances such as thymol, menthol and musk ambrette. It is used as a starting material in condensation reactions for the production of antioxidants. In Japan, m-toluidine is produced, on demand, by amination of m-cresol. Chlorinated m/p-cresol mixtures are used as disinfectants and preservatives. 2,4,6-trinitro-m-cresol can be used as an explosive [2].

High purity p-cresol is used as an intermediate in the manufacture of antioxidants with a wide range of applications. It is also a starting material for the production of UV light absorbers for polyethylene and polypropylene films and coatings. p-Cresol is used in the fragrance industry and in the production of anisaldehyde. Like o-cresol, m- and p-cresol are used as components in various dyes [2].

Cresol products are also used in fire resistant hydraulic fluids, as additives in lubricants, air filter oils, mixtures for ore flotation and fibre treatment, flame retardant plasticisers, metal degreasing and cutting oils, solvents for liquid extraction, agents for the removal

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of carbonisation deposits form internal combustion engines and as synthetic tanning agents. They also play a role in the paint and textile industry [2].

Xylenol mixtures are used as solvents, disinfectants and in ore flotation. Mixtures, especially those rich in 3,5-xylenol, are used in the manufacture of xylenol-formaldehyde resins. Xylenols with an o-methyl group are used to produce non-toxic plasticisers and trixylenyl phosphates for fire-resistant hydraulic fluids. 2,4-/2,5-Xylenol mixtures are raw materials for antioxidants. 2,6-Xylenol is used primarily to produce poly(phenylene oxide), or PPO resins, which have properties such as high impact resistance, thermal stability and fire resistance [2].

Xylenols are also the starting materials for polycarbonates, whose properties are similar to those of the PPO resins, pesticides and in the manufacture of disinfectants, antioxidants and industrial preservatives. Pure xylenols are also used in small amounts in the synthesis of dyes, pharmaceuticals and fragrances [2].

It is clear that phenolic products form an integral part of a number of diverse applications. The demand for these products is thus assured and their recovery is consequently commercially desirable.

1.3 Sources of Phenolic Compounds

Cresols were originally obtained only from coal tar. After 1945 they were also obtained from spent refinery caustics and since the mid-1960s they have been produced synthetically on an increasingly larger scale [1]. Synthetically produced cresol now provides approximately 65% of the requirements of the United States, Europe and Japan; only about 25% and 10% of the requirements are respectively met by cresol from coal tar and spent refinery caustics. The combined total output of cresol in these countries has however remained relatively constant over the last two decades at approximately 220 000 t/a [2].

Also significant is the amount of xylenols recovered from coal tar and spent refinery caustic, namely 30 000 t/a to 40 000 t/a [2].

1.3.1 Coal Liquors

Coal liquors and coal tars are formed in the carbonisation of coal for the production of smokeless fuels and as by-products of processes such as coal pyrolysis, pressure

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gasification and coke production. These coal liquors are initially distilled to yield light, middle and heavy oil fractions as well as a pitch residue. The light and middle oils are rich in phenol, the three cresol and six xylenol isomers, along with minor amounts of higher substituted phenols. Xylenols from bituminous coal tar are especially rich in the 3,5-xylenol isomer Higher substituted phenols include ethyl phenols and C_3- and C_4-substituted phenols [1].

The high temperature coke-oven tar obtained in the production of metallurgical coke is rich in cresols and xylenols. The manufacture of coke in by-product ovens typically results in the production of 40-60 litres of tar and light oil per ton of coal. The crude coal tar is distilled to yield light oil (~5%), middle oil (~17%), heavy or creosote oil (~17%) and pitch (~61%). The phenolic compounds typically represent 2-3 % of the original tar and are primarily present in the light oil (up to 200 °C boiling point) and the middle oil (200 to 250 °C boiling point) fractions [1].

Approximately 25% of the tar cresols produced in the United States and Western Europe are obtained from tars produced in Eastern Europe and from crude phenolic mixtures produced in South Africa [2]. The source of the South African phenolics is the liquid by-products obtained by Sasol Ltd. in pressure gasification of bituminous coal by the Lurgi process. These coal liquors are similar in composition to low-temperature tars i.e. 21.6 kg phenols and 3.1 kg cresols per ton of water-free bituminous coal [1].

In the United Kingdom, cresols are also produced from low-temperature coal tars obtained in the production of smokeless fuels, using the Coalite process [1].

Although the scale on which cresols and xylenols are recovered from coal tars has decreased continuously over the past 25-30 years, it is important to note that this is due to a decrease in the quantities of coal tars produced and not due to a decrease in the demand for phenolic compounds.

The decrease in the production of coal tars can be attributed to the following factors: the decline in the coke consumption of the iron- and steel-producing industry, which determines the supply of tar, and the increasing use in coke production of processes that lead to tars with lower cresol and xylenol contents [2]. Also, during the 1950s and 1960s coke was virtually replaced in many countries by petroleum and natural gas as raw materials for the chemical synthesis of organic compounds and ammonia [1].

The primary source of phenolic-rich coal liquors is thus the pressure gasification of coal. However, although the gasification of coal was developed to an advanced stage in the first half of the twentieth century, especially in Europe, in the last 30 years the changeover to natural gas and the gasification of oil and naphtha has resulted in a decline in the importance of the coal gasification. E.g. in 1957 more than 90% of the

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total gas production in the Federal Republic of Germany came from coal, of which approximately 15% was obtained by gasification. By 1975 only 20% of the total gas production came from coal and only 0.3% of this amount was obtained by gasification. I.e. the tar output from gasworks become largely insignificant, except in a few countries with special economic conditions, such as South Africa, Czechoslovakia and India [6].

The situation may change, however, as the gasification of coal to produce synthetic natural gas and syncrude should expand as the reserves of natural gas are depleted and the prices of oil and natural gas rise. This problem was already evident in many parts of the USA by the early 1970s, where shortages of natural gas became apparent. This resulted in the institution of research and development programmes aimed at producing alternatives to natural gas. These investigations were initially directed towards the production of gases from oil, but following the steep rise in the price of crude oil in the mid 1970s, the emphasis was shifted to coal as a starting material [6]. Emerging technologies are therefore currently aimed at the conversion of coal reserves to liquid and gaseous fuels.

An increase in the gasification of coal would yield more low-temperature tar, in which the content of the cresols and xylenols is much higher than in high-temperature coke-oven tar [2].

1.3.2 Synthesis

The synthesis of phenolic compounds has steadily increased since 1965, when the recovery of cresols from coal tar and spent refinery caustics became insufficient to meet the rising demand. Synthesis routes to phenol and the cresol isomers are well established and have been implemented commercially since the 1950s [2].

Synthetic routes to cresol have the advantage over recovery processes in that it is possible to manufacture high purity isomers with lower concentrations of the isomers that are in low demand than the concentrations contained in natural cresol sources. However, the raw material cost is much higher since the building blocks are phenol or toluene, which have high market values relative to the coal tars. Therefore, the recovery of substantial commercial quantities of phenolic materials from coal-based operations, combined with separations technology, could limit the synthesis of specific isomers. This will be especially true if a separation process can be developed to recover phenolic compounds with purities comparable to the synthetically produced compounds [1].

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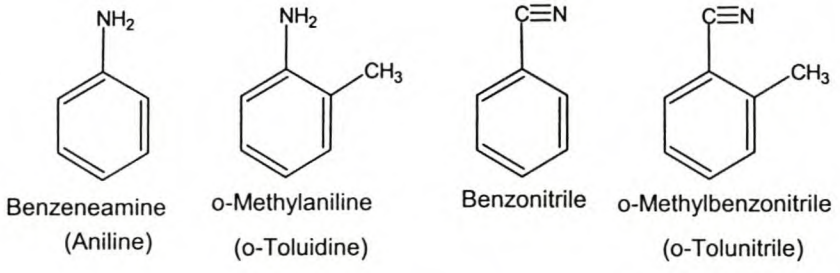
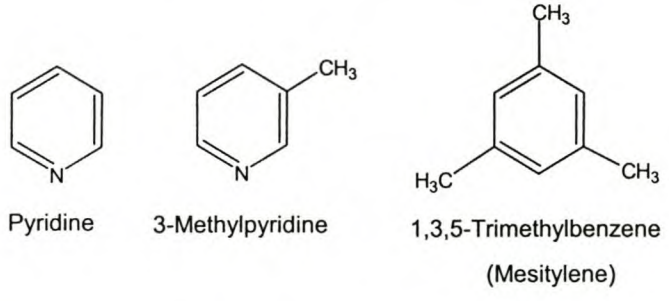
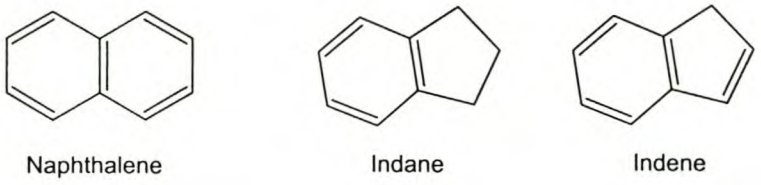
1.4 Factors Affecting Recovery of Phenolics

A process whereby phenolic compounds may be recovered from coal tars has long been sought. Unfortunately the separation of the phenolic compounds from the neutral oils and nitrogen bases also present in the liquors is complicated by the low relative volatilities between the phenolic compounds and various oils, the formation of both low- and high-boiling azeotropes as well as eutectics. For example, phenol, aniline and benzonitrile have boiling points (181.8, 184.4 and 191.0 respectively) that differ by only a few degrees. The difference in boiling points of m-cresol, o-tolunitrile and o-toluidine (202.3, 205.1 and 200.3 respectively) is also very small. The cresols form azeotropes with a number of compounds such as decane, 1-undecene, dodecane, 1,2,4,5-tetramethylbenzene, aniline, the toluidines and numerous pyridine derivatives, all of which may be present in the coal tar fraction [2].







Another factor contributing to the difficulty of the desired separation is that the tar fractions contain a considerable number of components, both phenolic and otherwise, in ratios that vary significantly. These variations depend not only on the starting material, but also on the process conditions and mode of operation used in producing the tars. The wide-boiling range of the tar fractions also complicates the choice of separation process.

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It is therefore clear that separation of the phenolic compounds from the neutral oils and nitrogen bases cannot be effected by a simple separation scheme.

As was discussed in Section 1.3, the greatest potential source of natural phenolic compounds in the present industrial context is the coal liquors formed as byproducts of the gasification of coal. Figure 1.4-1 illustrates the typical product streams obtained during the Lurgi pressure gasification of coal.

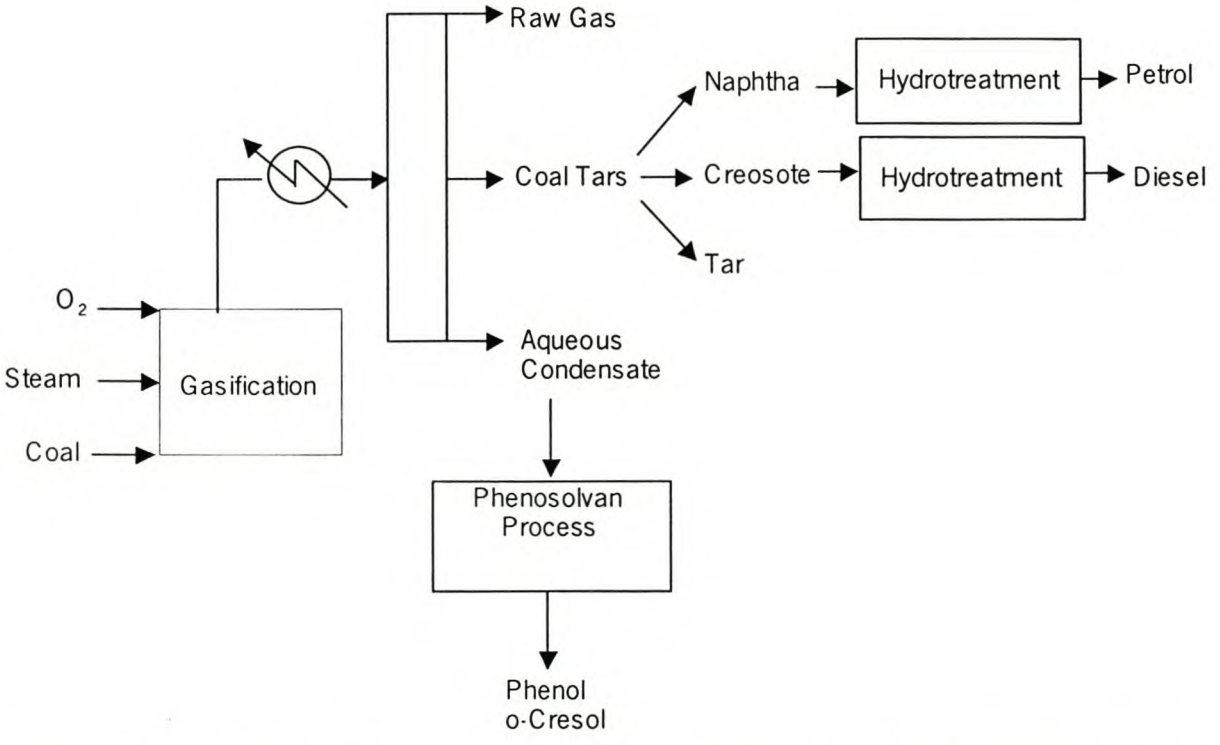

Figure 1.4-1 Schematic diagram of the coal liquors formed as byproducts of the Lurgi gasification process.

As can be seen from Figure 1.4-1, the gasification process yields two condensate streams, namely coal tar and a phenolic-rich water or gas liquor. This is true of most coal processing technologies, including coking and devolatilisation. The phenolic compounds in the gas liquor are typically extracted with a solvent such as an ether, ketone or light aromatic. After removal of the solvent, this mixture of phenolic compounds may be distilled to separate the phenolic fraction from pitch, which may contain dihydric phenols. The phenolic fraction can then be distilled to remove the water and residual volatile neutral oil. The resultant dried and depitched gas liquor extract contains far lower concentrations of neutral oils and nitrogen bases than the coal tar condensate stream. Typically, neutral oils and nitrogen bases account for 1.5-5%

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and 1.5-3% respectively of the gas liquor extract in comparison to the 50-70% neutral oil content and the 3-6% nitrogen base content of the coal tar [7].

While the gas liquor extract may be processed by any number of industrially established processes (the most common of which is the Phenosolvan process [8]), a satisfactory process for the industrial recovery of phenolic compounds from coal tar has yet to be discovered.

1.5 Project Definition

The ultimate goal of this project is to develop a process by which high purity phenolic compounds can be recovered from coal pyrolysis liquors. The purity of the final phenolic product must be comparable to that of synthetically produced and commercially available phenolic compounds. The recovery of the phenolic compounds must be high enough that the process is commercially viable. The impact on the environment must be minimal.

The process must be capable of handling feed streams which consist of a large number of components encompassing a wide boiling range (~180-240°C) and containing a variety of functional groups. The efficiency of the process must not be significantly affected by fluctuations in the ratios of the components in the feed.

Liquid-liquid extraction is a separation process capable of exploiting the structural differences between phenolic compounds and the wide range of neutral oils and nitrogen bases involved. It is a proven robust separation technique, which can handle large fluctuations in feed rates and compositions. As such, liquid-liquid extraction with one or more solvents is proposed as process for the separation of phenolic compounds from neutral oils.

The investigation of the proposed separation process will encompass the following:

1. Characterisation and representation of an industrial liquor, i.e.:
   - the identification of phenolic components, neutral oils and nitrogen bases present in a typical industrial coal tar fraction;
   - the compilation of a number of synthetic feed mixtures to represent various boiling-range fractions of the industrial mixture.
2. Commercial solvent selection, based on one of the representative synthetic feed mixtures, i.e.:

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- the use of model predictions to select commercially available solvents for the separation of phenolic compounds from neutral oils and nitrogen bases;
- the experimental confirmation, by means of batch extractions, of the predicted performance of the theoretically selected solvents.

3. Optimum solvent design, i.e.:
   - the theoretical design and, if commercially unavailable, synthesis of an optimum solvent;
   - the comparison of the synthesised solvent with commercially available solvents, by means of batch extractions using various synthetic feed mixtures.
4. Optimisation of the commercial solvent system by means of batch extractions, i.e.
   - the investigation and optimisation of solvent ratios and mixtures based on all the synthetic feed mixtures;
   - the experimental testing of the optimum commercially available solvent on the original industrial coal tar fraction.
5. Thermodynamic modelling of the batch extractions using the synthetic feed mixtures.
6. Conceptual process design and simulation, including solvent recovery.
7. Pilot plant testing of the proposed process on:
   - a synthetic feed stream;
   - an industrial coal tar fraction.

1.6 Aims

In general terms, the proposed process must have the following characteristics:

1. High degree of separation efficiency between phenolic compounds and neutral oils and nitrogen bases
2. High recovery of phenolic compounds, up to and including the xylenol isomers
3. Trivial solvent recovery
4. Negligible solvent losses
5. Minimal impact on the environment
6. Processing of a feed stream with a wide boiling range

The final separation process must satisfy the following specific requirements when implemented on pilot plant scale:

1. Final phenolic product purity after solvent recovery: >99.5% (mass)
2. Final product recovery >90% of feed phenolics

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1.7 Logic Flow Diagram of Project

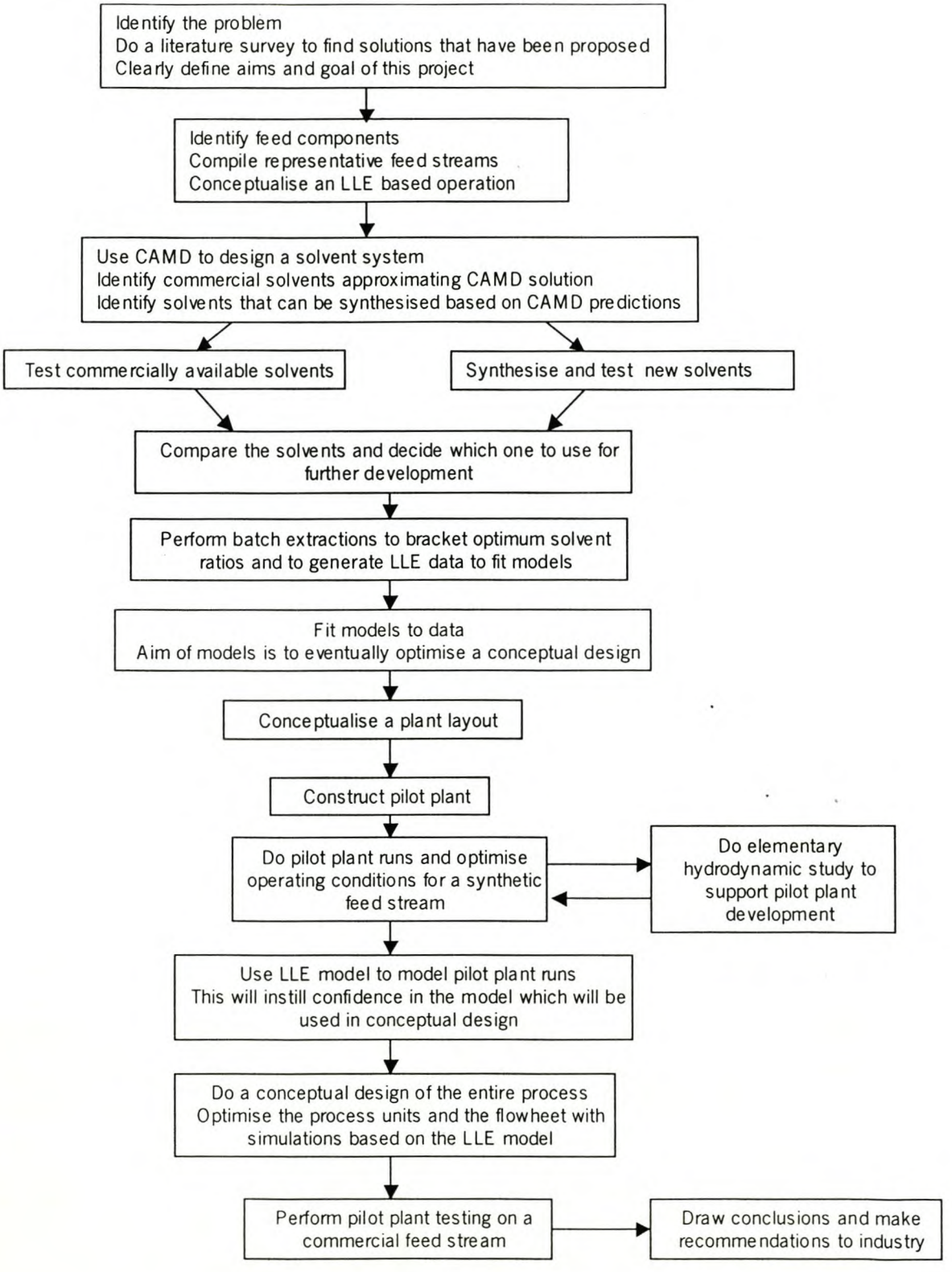

Figure 1.7-1 Logic Flow Diagram of project

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CHAPTER 2. LITERATURE SURVEY

2.1 Liquid-Liquid Extraction

Liquid-liquid extraction, or solvent extraction, is a mass transfer operation in which a homogenous liquid solution (feed) is contacted with a second immiscible or nearly immiscible liquid (solvent) that has been selected to preferentially extract a desired compound (solute) from the feed. The feed can simultaneously be contacted with a third liquid (antisolvent, counter-solvent or washing solvent), which is immiscible with the solvent and miscible with the feed.

Two liquid phases are formed as a result of this contact: the extract or solvent phase which contains the extracted solute, and the raffinate or antisolvent phase which consists of the residual feed stream and antisolvent. The two liquid phases are immiscible and can therefore easily be separated, thereby effectively separating the desired solute from the undesired compounds originally present in the feed.

A second separation step must necessarily be employed to recover the extracted component from the solvent. Therefore, liquid-liquid extraction is used only for separations which cannot easily or economically be achieved in a single step. Such separations generally involve [9]:

- dissolved or complexed inorganic substances in organic or aqueous solutions;
- the removal of a component present in very small concentrations;
- the removal of small concentrations of a high-boiling component in a waste stream;
- the recovery of heat-sensitive materials where extraction may be less expensive than vacuum distillation;
- close-melting or close-boiling liquids, where solubility differences can be exploited;
- mixtures which can be separated according to chemical type, rather than relative volatility;
- mixtures that form azeotropes;
- components prone to polymerisation at high-temperatures.

The coal tar fractions from which the phenolic compounds are to be recovered contain close-boiling as well as close-melting liquids, a mixture of components of different chemical type which form azeotropes and tend towards polymerisation at high temperatures. Liquid-liquid extraction is thus strongly indicated as a technique for the separation of phenolic compounds from neutral oils and nitrogen bases.

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2.2 Liquid-liquid Extraction Processes

Liquid extraction has been practised since at least the time of the Romans, who separated gold and silver from molten copper using lead as a solvent. However, it was not until the early 1930s that the first full-scale liquid-liquid extraction process began operation. This was the process invented by L. Edeleanu in which liquid sulphur dioxide was used as a solvent to selectively remove aromatic and sulphur compounds from liquid kerosene, resulting in a cleaner-burning kerosene. Today, liquid-liquid extraction is a relatively mature separation operation and, although not as widely applied as distillation, absorption and stripping, it is used as a commercial separation process in a wide variety of applications. It has been successfully implemented in industries as diverse as the petroleum, chemical, food and pharmaceutical, metal, nuclear and environmental industries. The growing demand for temperature-sensitive products, higher-purity requirements, more efficient equipment, and availability of solvents with higher selectivity should ensure that the importance of liquid-liquid extraction as a separation process will continue to grow [9].

2.2.1 Petroleum Industry

The need to separate mixtures of aliphatic and aromatic hydrocarbons provided one of the first large-scale applications for solvent extraction. The particular advantage of solvent extraction in this case was that it represented a means of separating groups of components of similar chemical type.

2.2.1.1 Lubricating oil extractions

The viscosity, odour and high volatility of crude petroleum thwarted early attempts to exploit its lubricating properties. The required viscosity could be obtained by means of distillation, but the aromatic, resinous and asphaltic materials content remained. This resulted in a low resistance to the formation of sludge, acid and carbon.

Aromatics can be removed from lubricating oils and kerosenes using a solvent that preferentially dissolves aromatic compounds from a mixture of hydrocarbons. Two streams result: the raffinate, consisting of nominally aromatics-free hydrocarbons, and the aromatics-rich solvent. The residual aromatics content of the raffinate can be reduced to an economically acceptable level by a large number of extraction stages and by using surplus solvent. The separation of aromatics from naphtenes and isoparaffins in lubricating oils improves the viscosity-temperature relationship, while the removal of

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aromatics from fuel improves the clean burning properties. In both cases the end product is a high-purity raffinate.

Sulphuric acid was used in the first effective liquid-phase treating process for crude lubricating oil. This process was not a true solvent extraction process in that it selectively removed unstable components by means of chemical reaction. It did however effectively upgrade the oils and was widely used by refineries until disposal of the acid sludge became a major problem, ultimately leading to the obsolescence of acid treating.

In the early 1900s, L. Edeleanu identified aromatic and unsaturated hydrocarbons as the undesirable components in crude lubricating oil. Liquid sulphur dioxide was identified as an appropriate solvent for selectively removing these components and was successfully used in the refining of kerosene from 1911 [10].

Economic and environmental disadvantages of this process included high solvent losses and the need to exclude water from the system in order to minimise corrosion and prevent chemical reaction of SO_2 with the hydrocarbons present. As a result the process was eventually discontinued.

Subsequently, benzene was added to the sulphur dioxide, leading to an increase in solvent capacity, a slight decrease in selectivity and the processing of a greater variety of paraffinic feeds. It also unfortunately resulted in the need for steam stripping facilities, thereby producing benzene-water-sulphur dioxide mixtures that increased the potential for corrosion [10].

These early applications recognised the advantages of countercurrent operations, although it was still only achieved by means of separate mixer-settler stages. Vertical towers with continuous countercurrent flow later became the standard method of contacting.

Further developments in the automotive and aviation engines required quality levels in lubricating oils and fuels beyond those attainable with SO_2, both with and without benzene. A number of compounds were investigated in the 1930s and as a result phenol, furfural , nitrobenzene and dichlorodiethyl ether were adopted for the extraction of lubricating distillates.

The phenol extraction process was first commercialised in 1930 and has been used extensively ever since, being second only to furfural in world-wide plant capacity. Advantages include the high solvent power of phenol, the low solvent losses (0.03% on solvent turnover) and the maintenance of convenient extraction temperature ranges (50-

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100°C) by the addition of water. Problems include the high melting point and toxicity of phenol, resulting in the necessity of special handling facilities [10].

Furfural is the other dominant solvent used in lubricating oil extractions. It is prone to decomposition and, as such, the feedstock must be thoroughly deaerated and recovery temperatures must be kept below 220°C in order to prevent high solvent losses, corrosion and fouling of equipment. The relative instability of furfural has however been overcome by detailed design, materials of construction and care in operation, resulting in an economical and flexible method of solvent extraction.

N-methyl pyrrolidone (NMP) is highly selective for aromatics and has more recently been applied to lubricating oil refining. It is thermally stable and solvent losses are low. Oil solubility is controlled by varying the temperature and water content of the solvent. No feed pretreatment is required and the water can easily be removed from the system either by means of absorption or distillation. Two commercial processes have been developed. Both employ countercurrent extraction with multiple stages of extract and raffinate stripping using either steam or nitrogen as the stripping agent [10].

NMP has advantages in safety and physical properties over phenol and stability over furfural. Its superior selectivity can be used either to increase throughput or to reduce the fuel required per unit of throughput.

Residual feedstocks for lube production can only be utilised after removal of asphaltic material. Separation by means of distillation is not viable as the boiling point exceeds the decomposition temperature, even under vacuum. Extraction with liquid propane was thus developed as an alternative method of separation and remains the primary upgrading step for residues prior to refining. Many process improvements have been applied since the first propane deasphalting plant was constructed in 1935, including the change from mixer-settler equipment to continuous countercurrent extractors.

None of the processes described thus far are capable of processing residual streams containing large amounts of asphaltic materials. The Duo-Sol process combines propane with a polar solvent, "selecto" - a blend of cresol and phenol - thereby enabling it to handle both distillate and residual feedstocks. Propane rejects the asphalt while selecto removes the aromatic compounds. However, the use of two solvents involves more operating variables and a more complicated recovery design than is the case with a single solvent. Investment and operating costs are thus generally higher than with separate deasphalting plus single-solvent plants. Therefore, while Duo-Sol plants were widely used between 1935 and 1950, no new ones have been built since the 1960s [10].

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2.2.1.2 Benzene, Toluene and Xylene (BTX) Production

Although great volumes of broad-cut raffinates are still required for fuels and lubricants, the development emphasis shifted to the production of high purity aromatic extracts in the 1950s. This resulted in several commercial processes for the manufacture of BTX.

The first efficient method for the recovery of aromatics was the Udex process, which used a glycol-based solvent. This was introduced in 1952 and was superior to existing technologies as it could directly treat a wide-boiling feedstock, without expensive prefractionation, and still produce BTX products of unusually high purity. Originally, the process used aqueous diethylene and triethylene glycol (DEG and TEG). Both DEG and TEG are very selective, but DEG has a much lower capacity for benzene. As there is a growing demand for petrochemicals and high-octane fuel, greater extraction capacity is needed. The trend in industry was thus to use TEG instead of DEG. Around 1968, researchers at the Union Carbide Corporation identified tetraethylene glycol (tetra) as having a higher capacity than TEG or DEG. The recoveries of benzene, toluene and xylene with tetra are typically 100%, 99.5% and 95% respectively [10].

The Sulfolane process was developed by the Royal Dutch / Shell group and was first applied commercially in 1961. The process is based on the polar solvent Sulfolane (tetrahydrothiophene-1,1-dioxide), which is extremely selective. Due to the solvent's high boiling point, feedstocks with boiling ranges of up to 250°C can be accommodated. Its high melting point can be considerably reduced by the addition of a small percentage of water or hydrocarbons. Extraction takes place countercurrently at a temperature of about 120°C. Extract purity is low after an extraction step alone. It is possible to use Sulfolane in an extractive distillation process as well. Such a process is used when only one aromatic must be recovered from a feedstock with a narrow boiling range. For wider-boiling feedstocks covering more than one carbon number, extractive distillation alone is not feasible. A combination of extractive distillation and extraction is then used. The available feedstock, desired aromatics purity and recovery will determine which scheme is most appropriate [10].

NMP, which is also used for BTX extraction in the Arosolvan process, can be used without an additive only for the extraction of small amounts of aromatics. When dealing with reformates and hydrogenated pyrolysis liquors, a mixing component must be added. As the NMP has a high capacity and low selectivity, the mixing component must have a high selectivity and low capacity. The addition of a mixing component can be used to advantage as, by varying the type and quantity thereof, the solvent can be adapted and optimised for various duties. Water and monoethylene glycol, both of which have a high polarity, are used in the Arosolvan process. Each of the two mixing components requires a different process due to differences in their boiling points and

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heat requirements. Another difference is the application of a pentane antisolvent in the NMP-water process to ensure the maintenance of a two-phase system and a low recycle rate. Higher investment costs are thus compensated by lower operating costs. The aromatics purity is the same in both cases.

The solvents used in the Sulfolane, Udex and Arosolvan processes have a number of common characteristics. They all have densities and boiling points higher than the material to be extracted and are all to a greater or lesser degree polar molecules that are water soluble [10]. The processes involved all rely on liquid-liquid extraction coupled with extractive distillation - an arrangement which allows the selective properties of the solvent to be used for the removal of the last traces of non-aromatics in the extractive distillation step. An alternative purification procedure would be to use a second non-aromatic solvent [11].

Such a process was developed in France in the 1960s. Here the primary solvent was dimethylsulphoxide (DMSO) containing a small percentage of water. The selectivity and low viscosity of the solvent allows the extraction to take place entirely at ambient temperature.

In the 1970s N-formylmorpholine (NFM) was used as a solvent for BTX recovery by Krupp-Koppers and Snamprogetti in the Aromex and Formex processes respectively. In both cases the NFM contains water, which improves selectivity but also makes hydrolysis to morpholine and formic acid formation possible. Fortunately, as the hydrolysis reaches an equilibrium that is strongly biased in the favour of the solvent, the concentration of the acid and base are very small [11].

The production of BTX and lube oils remains the main application of extraction in the petroleum industry today. Some specialised applications that are being evaluated are: the removal of naphtenic acids from crudes prior to atmospheric distillation, the removal of phenolics from desalter water and coal tar distillates, the removal of organic compounds and polymers from caustic wash streams in refineries and the removal of solvent and acids from alkylation processes. Several of these are currently in the pilot plant stage of development and will proabably be commercialised over the next few years [12].

It is clear that liquid-liquid extraction has proved to be an economically viable means of improving product purity and reducing energy consumption in the petrochemical industries - despite the fact that solvent recovery invariable involves costly distillation. This can be attributed to careful process integration and the development and large-scale use of new types of extractors.

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2.2.2 Chemical Industry

The chemical industry, and in particular those sections involved in the production of specialty chemicals, fine chemicals and fibres, remains the main industrial area for both the application of solvent extraction to current production as well as development of new extraction processes [12].

The caprolactam process, for example, remains an important source of nylon today. The production of high-purity fibre-grade caprolactam can be achieved with vacuum distillation and crystallisation from water, but the favoured route is solvent extraction - not only for the final purification of the caprolactam monomer, but also for the recovery of the intermediate product cyclohexanone oxime. In cases where the caprolactam is produced from caprolactone and not cyclohexanone oxime, solvent extraction with the process cyclohexane is still used to recover unreacted cyclohexanol and cyclohexanone from aqueous liquors [13].

New developments involve new reaction routes to the monomer that minimise the formation of by-products and have an impact on the extraction steps needed for purification. Other developments involve the study of different contactor designs.

Liquid-liquid extraction is currently being used in the preparation and purification of compounds other than caprolactam. Examples include the washing of solvents from reactor effluent streams and the washing of residues to recover cobalt catalyst salts.

Substantial savings in plant investment and operating costs are possible with the implementation of liquid-liquid extraction in the commercial production of anhydrous acetic acid. Recovery of acetic acid from water was proposed by Göring in 1883 and, as such, is one of the oldest applications of solvent extraction. The acid is recovered from an aqueous phase, thereby greatly reducing the amount of water that must be distilled in order to produce anhydrous acid. This process is widely applicable as numerous manufacturing processes yield aqueous waste or by-product streams containing acetic acid. These include the manufacture of cellulose acetate, aspirin, and camphor. In addition, various manufacturing methods for acetic aced involve separation from water [14].

Rhone-Poulenc have also developed a new process for the recovery of acetic acid from dilute aqueous solutions. The solvent is a mixture of butyl alcohol, with ammonium and butyl acetate. The solvent extract is neutralised with ammonia followed by thermal decomposition of the resulting ammonium acetate and then distillation.

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Another example where solvent extraction is more favourable economically than distillation is in the manufacture of acrylic fibres. Here, as in the previous process, a mixed solvent, such as benzene and methyl ethyl ketone, offers advantages for the recovery of acrylic acid from aqueous solutions [12].

Extraction processes for organic materials are not all based on relatively unspecific physical interactions between the solute and solvent. There can be a definite chemical reaction with the solvent. For example, xylenes react rapidly and reversibly to form complexes with boron trifluoride in the presence of liquid hydrogen fluoride. Under the correct conditions this behaviour can be used to separate m-xylene from its more marketable isomers because the m-xylene complex is much more stable than the others and is preferentially soluble in the excess hydrogen fluoride [12].

2.2.3 Other Industries

Extraction is a major technology in the production of primary metals, principally copper, nickel and cobalt. The main innovations are in the development of new and better solvents that are more selective, easier to regenerate and that have faster kinetics.

The most significant application in the food and pharmaceutical industry is the recovery and purification of the products of fermentation, particularly antibiotics and vitamins.

There is little information available on the commercial use of solvent extraction in the manufacture of drugs and natural products in the pharmaceutical industry. The process is widely used, however, because many pharmaceutical products are heat sensitive. This feature rules out separation methods such as distillation or evaporation.

A growing area of application is the biotechnology field, where extraction is used to purify genetically engineered products.

An entirely new application for solvent extraction, which intersects all industries, is in the environmental area. This is due to the increase in the demands placed on industry to comply with environmental regulations. The largest untapped potential for the application of solvent extraction is probably the removal of organic contaminants from waste waters. A particular strength of extraction in these applications is its ruggedness - it can handle solids, greases, oils and aggressive chemicals that often occur in these streams without the degradation and plugging problems of technologies such as adsorption or membranes. It is also flexible over the wide range of flow rates and concentrations that must be handled.

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2.2.4 Future Applications

Because of the high investment associated with petroleum refining process units, major changes occur relatively infrequently and only after extensive development. Most advances within a given process are achieved by stepwise improvement to increase throughput, decrease solvent losses and reduce energy consumption. Economically, it is often impossible to justify liquid-liquid extraction for existing operating plants. This is however expected to change as regulations become more stringent. For new plants or major plant expansions, extraction can often be justified as it represents only a small fraction of the total plant investment.

Since future energy costs are predicted to account for an ever-increasing fraction of total manufacturing costs, processes requiring minimum energy should become dominant. The prime use of energy in solvent extraction is for solvent recovery by means of distillation. Solvents offering improved selectivity and capacity and therefore reduced treatment rates, will thus be favoured. High-efficiency contacting equipment using rotating or oscillating components can similarly reduce solvent treatments by increasing the number of theoretical stages available.

The improved process control achievable with computers should reduce solvent losses to very low levels so that solvent cost becomes a less significant factor. Solvents rejected on this basis in the past may therefore become much more attractive if they meet other key requirements [12].

2.3 Liquid-liquid Extraction Equipment

Liquid-liquid extraction lends itself to a wide range of applications. There is a correspondingly large variety of liquid-liquid extraction devices. Equipment similar to that used for absorption, stripping and distillation is not often used as it is inefficient unless liquid viscosities are low and the difference in phase density is high. Centrifugal and mechanically agitated devices are preferred.

Extraction apparatus can be classified in the following groups [15]:

1. Columns without energy input
2. Columns with mechanically assisted agitation such as:
    a. Columns with pulsed liquid or pulsed internals
    b. Columns with rotating internals
3. Centrifugal Extractors
4. Mixer-settlers

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2.3.1 Columns without Energy Input

2.3.1.1 Spray columns

The simplest extractor is the spray column (Figure 2.3-1 a and b). A distributor for the light phase is located at the bottom of the empty column. Due to the difference in density relative to the continuous heavy phase, the light phase rises and coalesces in the upper settling space to give a continuous layer. The interface between the heavy and light phases is kept at a constant level by controlling the bottom discharge. The converse is possible if the heavier liquid phase is the dispersed phase. The distributor is then located at the top and the phase boundary at the bottom of the column. The spray column can unfortunately only be used for very simple separation problems as the number of separation stages achieved is very small. High throughput can be achieved [15].

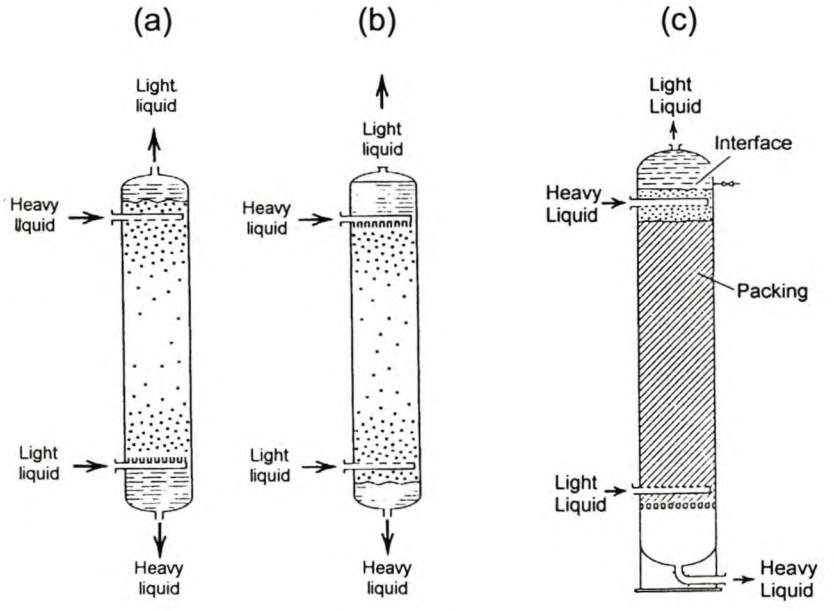

Figure 2.3-1 : a) Spray Column, light phase dispersed,
b) Spray Column, heavy phase dispersed [9]
c) Packed Column, light phase dispersed [16]

2.3.1.2 Packed Columns

The axial mixing characteristic of spray columns can be significantly reduced, although not entirely eliminated, by the addition of packing to the column (Figure 2.3-1c). The same packing is typically used as in distillation and absorption, although the choice of

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packing is more critical - it is preferable for the material to be wetted by the continuous phase [9]. Droplets are formed on entry of the dispersed phase to the packed bed. The packing improves mass transfer by breaking up large drops to increase interfacial area and promotes mixing in drops by distorting droplet shape. High throughput can also be achieved. However, the column is less efficient than staged devices as mass transfer is mainly through formation of the new interfacial area and backmixing is significant. It is therefore used only for separations that require few steps [15].

2.3.1.3 Sieve-plate Columns

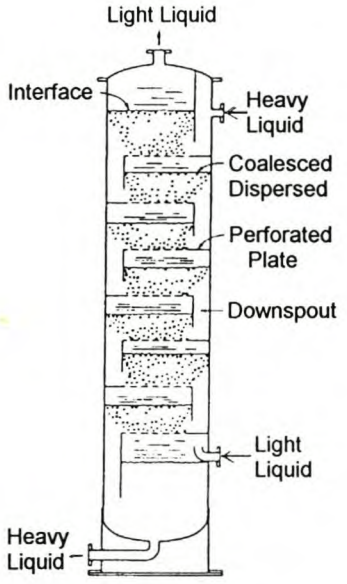

Figure 2.3-2: Sieve plate column, light phase dispersed [16].

Sieve plates in a column also reduce axial mixing and achieve a more stagewise type of contact. The dispersed phase may be either the light or heavy phase. In the first case, the dispersed phase coalesces under each plate to give a continuous layer, which is redispersed as it rises through the holes in the tray to the next higher stage (see Figure 2.3-2). The continuous phase flows through downcomers at each stage in a manner analogous to liquid flow in a distillation column. If the heavy phase is dispersed, upcomers are used for the light phase.

Extraction rates are high in sieve-plate columns if they are operated in the proper hydrodynamic flow regime. The dispersed phase droplets coalesce and reform on each stage, and, in so doing, prevent the formation of radial concentration gradients through the column. As a result, this type of column is an improvement on the packed column. Unfortunately, the distribution of coalesced droplets on the surface of the sieve plates is

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often irregular. The plate efficiency is thus very low and only reaches maximum values of 10-15% in rare cases. Sieve-plate columns also have the same limitations as distillation columns: flooding; entrainment and, in some cases, weeping. Additional problems such as scum formation at interfaces are characteristic of all types of extraction devices.

Despite low stage efficiency, sieve-plate columns have been built and successfully operated for diameters larger than 4.5 m [9].

2.3.2 Columns with Mechanically Assisted Agitation

Gravitational forces are often inadequate for proper phase dispersion and the creation of turbulence, especially when surface tensions are high and density differences between the two liquid phases are low. Mass transfer between the liquid phases can be substantially improved if the system is supplied with energy, either in the form of pulsation or by means of moving internals [9].

2.3.2.1 Pulsed Columns

Pulsed Sieve-Plate Column

The simplest pulsed column is the pulsed sieve plate column (Figure 2.3-3) in which the entire liquid content of the column is agitated by a piston pump or diaphragm pump. Both liquid phases are alternately forced through the holes of the sieve plates by the rhythm of the pulsation, thereby obviating the need for downcomers. The dispersed phase does not coalesce above or below the plates to give a continuous layer. The drops are flung off the plate by the pulsation shock faster than would be possible as a result of density difference alone. This results in a fine, uniform drop distribution and thus enlarges the mass transfer area. Applications are limited by the physical properties of the components in the extraction system - systems which emulsify easily cannot be processed. The use of pulsed columns is generally limited to small and medium throughputs. For very large throughputs, the pulsed volume and pulsing power become very high and cause uncontrollable difficulties with the pulsing pump. The plate material is also critical as it has a significant effect on drop formation and therefore separation efficiency. The plate material and continuous phase must be selected so that the plates are wetted by the continuous phase and not the dispersed phase [15].

Pulsed sieve-plate columns were widely applied in the nuclear industry in the 1950s, but their popularity declined because of mechanical problems and the difficulty of

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propagating a pulse through a large volume [9]. More recently, however, pulsing units for large column diameters have been developed. Also, BASF has developed pulsed sieve-plate columns with larger free areas, in order to facilitate their use in applications requiring greater throughput [15].

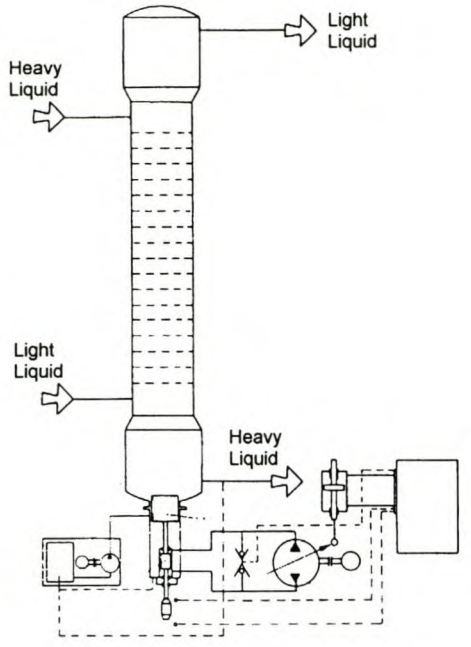

Figure 2.3-3: Pulsed Sieve-Plate Column [17]

Reciprocating-Plate Columns

The reciprocating-plate column was developed to handle large throughputs. In this type of column, the pulsing pump is eliminated by making the plates, and not the liquid, reciprocate. As with the pulsed sieve plate column, the liquid undergoes oscillating motion relative to the plate, but the column diameter is limited only by mechanical considerations [15].

Two different versions of the reciprocating-plate column are commercially available. In the Karr column (Figure 2.3-4b), sieve plates are mounted on a central shaft. The complete pack is moved up and down, driven by an eccenter. The vibrating plate extractor (VPE), developed by Prochazka (Figure 2.3-4a), is a modification of the Karr extractor. In this column a segment of each plate is cut off, allowing free passage of the continuous phase. This enables the use of smaller holes on the sieve plate. The

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segments are mutually offset at 180 degrees, so that a virtual cross flow is generated on each plate [15].

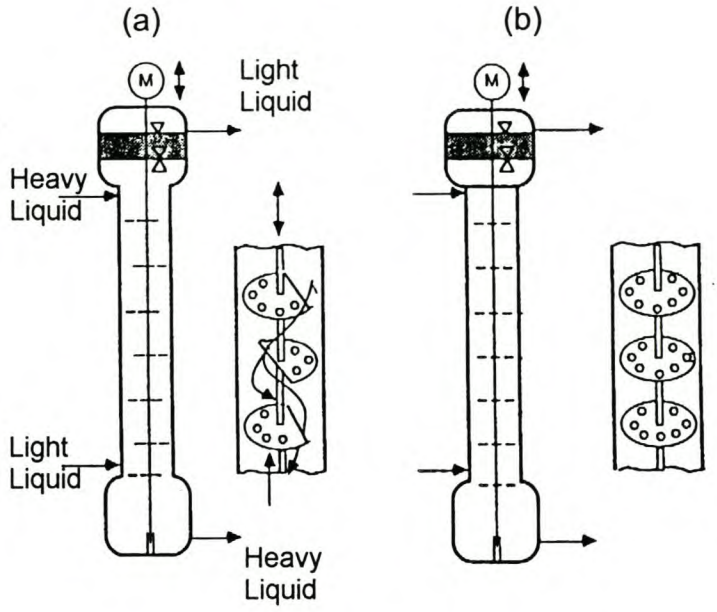

Figure 2.3-4: Reciprocating plate columns a) VPE column b) Karr column [15]

2.3.2.2 Columns with Rotating Internals

The most important mechanically agitated columns are those that use rotating agitators, driven by a shaft that extends axially through the column. The agitators create shear-mixing zones, which alternate with settling zones in the column. The various agitated columns differ primarily in the mixers and settling chambers used [9].

Scheibel Column

In the Scheibel column (Figure 2.3-5a), countercurrent liquid phases are contacted at fixed intervals by unbaffled, flat-bladed, turbine-type agitators mounted on a vertical shaft. Knitted wire-mesh packing is installed between the mixing zones to create unbaffled separation or calming zones in which coalescence is induced. The mesh material is wetted by the dispersed phase [15]. For columns with diameters larger than 1 m, outer and inner horizontal annular baffles are added to divert the vertical flow of the phases in the mixing zone and to ensure complete mixing. For systems with high interfacial tension and viscosities, the wire mesh is removed [9].

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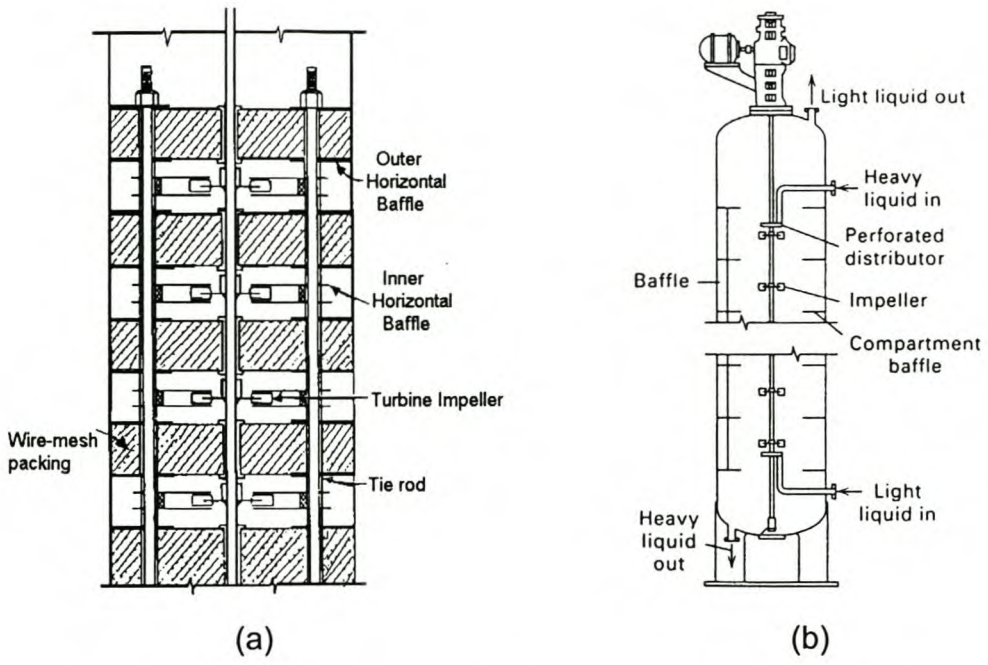

Figure 2.3-5: (a) Second Scheibel column with mesh packing [18]. **(b) Oldshue-Rushton column** [9].

Oldshue-Rushton extractor

The Oldshue-Rushton extractor (Figure 2.3-5b) consists of a column with a series of compartments separated by annular outer stator-ring baffles, each with four vertical baffles attached to the wall. The centrally mounted vertical shaft drives a flat-bladed turbine impeller in each compartment [9].

Rotating Disc Contactor (RDC)

In the RDC (Figure 2.3-6a), stator rings are mounted at close intervals on the inside wall of the column. Disks are fitted on a rotating shaft so that the disks and rings alternate. The drops of the dispersed phase are centrifugally flung off the rotating disks onto the stator rings where they are slowed down and deflected. As a result, excellent drop distribution is achieved. Care must however be taken to prevent emulsification at too-high rotational speeds. As in pulsed columns, the wetting behaviour also influences drop formation in the RDC, and should be taken into account when selecting a material for the column internals. The separation efficiency in the RDC decreases sharply with increasing diameter. Nevertheless, successful columns of up to 3.5 m in diameter have been constructed. The RDC is probably the most extensively used liquid-liquid extraction device, with hundreds of units in use by 1983 [15].

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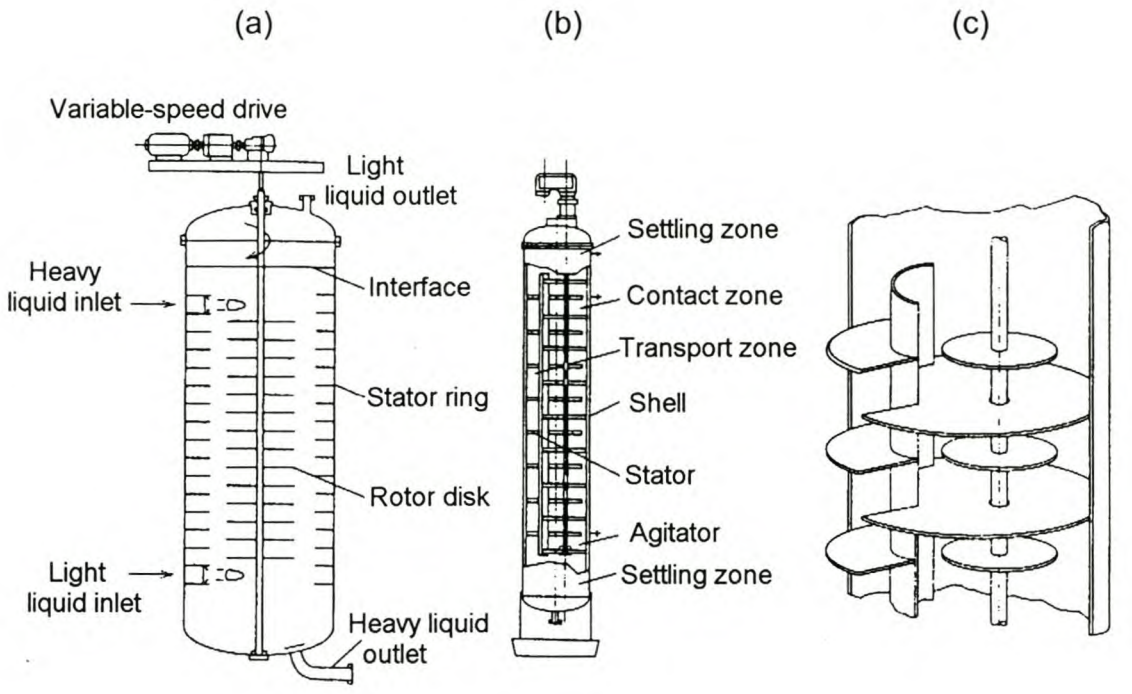

Figure 2.3-6: a) Rotating-disk contactor (RDC)
b) Asymetric Rotating-disk contactor (ARD)
c) Section of ARD contactor [9]

Asymmetric Rotating Disc Extractor (ARD)

The ARD extractor (Figure 2.3-6b) is a modification of the RDC concept and has been in industrial use since 1965. In the ARD column, the rotating shaft bearing the disks is positioned asymmetrically [9]. A vertical sheet separates the extractor into a mixing zone and a transport zone. In order to reduce backmixing, the stator rings of the RDC are replaced by closed partition disks across the entire column cross section. The opening for liquid flow is the vertical cross section between the partition sheet and the column wall. The ARD is suitable for large throughputs [15].

Kühni Extractor

Another extractor based on the Scheibel concept is the Kühni extractor (Figure 2.3-7). The mixing element is a double-entry radial-flow shrouded turbine impeller. Perforated stator plates separate the extraction stages and reduce backmixing. This residence time in the column can be adjusted by varying the free area of the stator plate. For columns of diameter greater than 3 m, three turbine-mixer shafts on parallel axes are normally provided to preserve scale-up. Three hundred of these extractors were in use, mainly in Europe, by 1983 [19].

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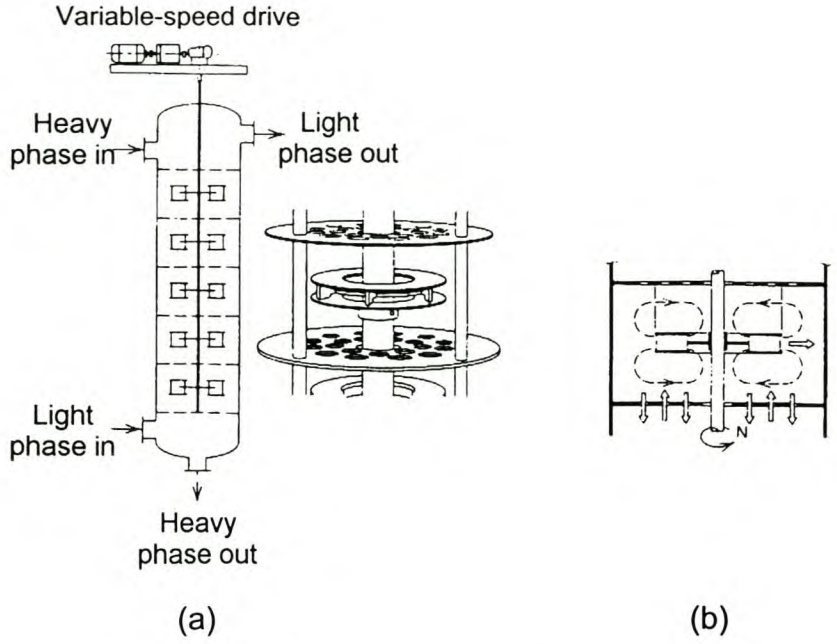

Figure 2.3-7: a) Kühni column, b) flow pattern in Kühni column [9]

Graesser Raining-Bucket Contactor (RTL)

The RTL (Figure 2.3-8) was developed in the late 1950s, primarily for extraction process involving liquids of small density difference, low interfacial tension, and a tendency to form emulsions. This novel contactor consists of a series of disks mounted inside a shell on a central horizontal rotating shaft, with a series of horizontal C-shaped buckets fitted between and around the periphery of the disks. An annular gap between the disks and the inside of the shell allows countercurrent longitudinal flow of the phases. Dispersing action is very gentle with each phase cascading through the other in opposite directions toward the interface, which is maintained close to the equatorial position [9].

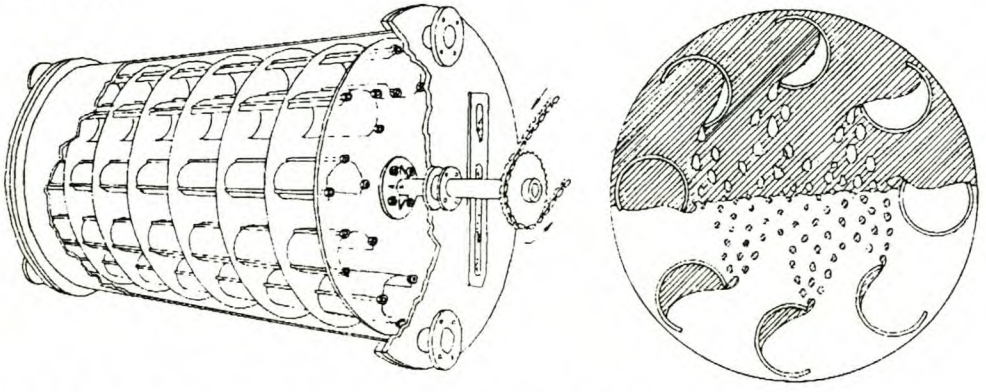

Figure 2.3-8: Graesser raining-bucket (RDL) extrtactor [15].

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Self-stabilising High Efficiency (SHE) Extractor

The SHE extractor (Figure 2.3-9) is equipped with alternating mixing and phase-separation zones. Conventional blade mixers are used for mixing. Rotationally symmetrical conical internals are located between the mixers. The apex of the conical internals point in the direction of flow of the dispersed phase. The effect of this design is that the dispersed phase partly coalesces [15].

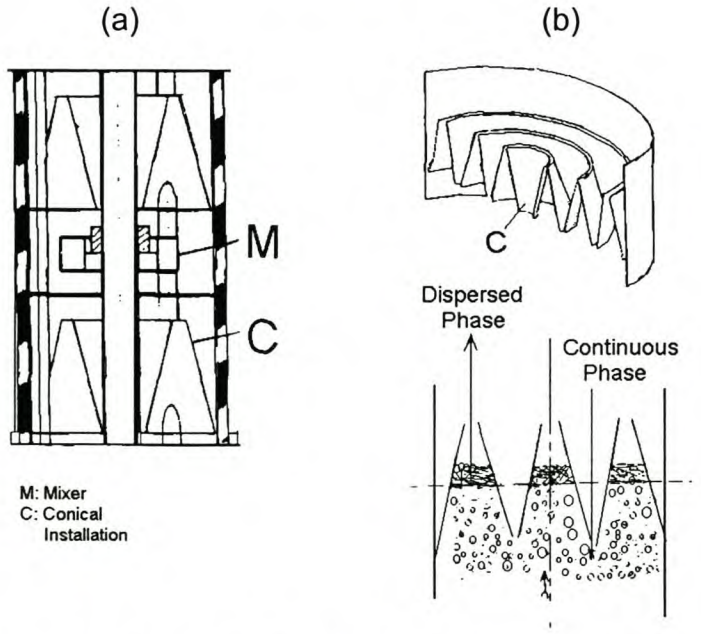

Figure 2.3-9: a) SHE extractor; b) Controlled phase flow in conical installations [17].

In general, pulsed and rotating columns have a better drop dispersion and greater mass transfer area than the simple packed and sieve-plate columns. As a result, separation efficiency is much better, but fluid dynamic conditions more complicated. Concentration profiles are distorted by backmixing of the continuous phase. The velocity distribution of the dispersed phase is also distorted. Ideal countercurrent flow can thus not be achieved. Another drawback is that coalescence causes an uneven drop size distribution. This interference is more apparent with increasing column diameter, especially in stirred columns [15].

2.3.3 Centrifugal Extractors

A number of industrial centrifugal extractors have been available since 1944, when the Podbielniak (POD) extractor was successfully applied to penicillin extraction. In the POD extractor (Figure 2.3-10a) sieve trays are concentrically arranged as a compact

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rotor on a high-speed shaft. The heavy phase is fed to the extractor via the shaft and moves outwards due to centrifugal force. The light phase moves in the opposite direction. Similar to columns, either the light or heavy phase can be dispersed into drops, as desired. Liquid inlet pressures of 4 to 7 atm are required to overcome pressure drop and centrifugal force. As many as five theoretical stages can be achieved in one unit [9].

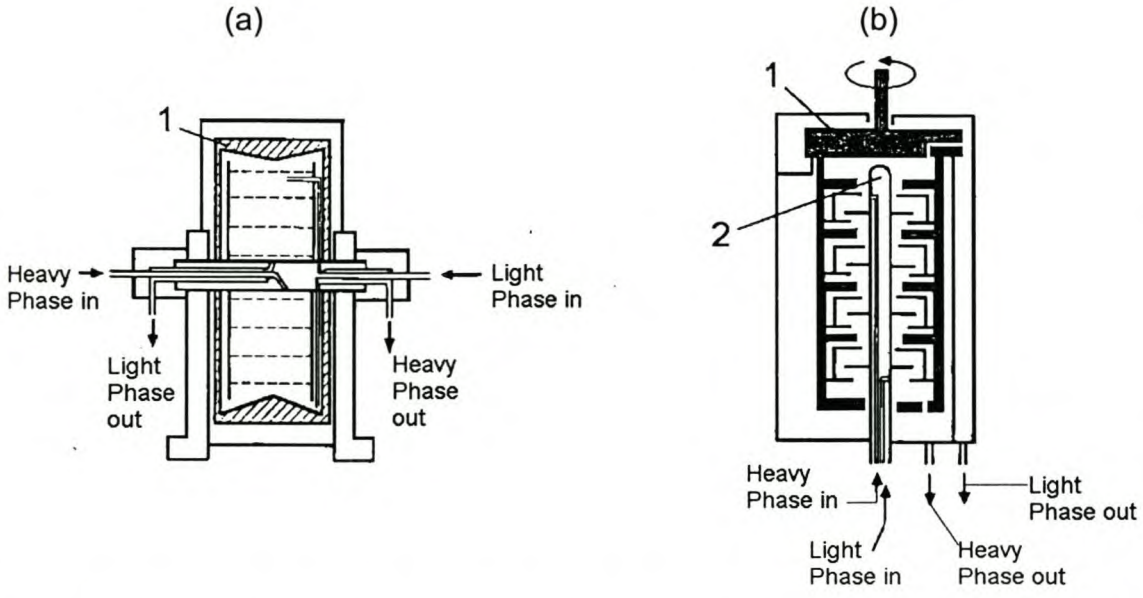

Figure 2.3-10: a) Podbielniak extractor; b) Robatel extractor; (1: rotor; 2: stator) [15]

The Robatel centrifugal extractor (Figure 2.3-10b) is based on a totally different principle and allows a greater number of stages. Disks serving as the mixing element are centred on a vertical stator. The housing is divided by annular disks into a number of stages and rotates around the central shaft. Each stage consists of a mixing chamber and a settling chamber. The disks each dip into the mixing chamber.

Centrifugal extractors are much more complex than columns, their investment and maintenance costs are correspondingly high. They are therefore used only when columns cannot be used for a given separation e.g. when the density difference between two phases is insufficient to produce a countercurrent flow under gravity.

The centrifugal extractor has an extremely small operating volume and a short residence time. These advantages can be desirable if expensive solvents or substances of limited stability are used [15].

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2.3.4 Mixer-Settlers

Countercurrent flow and ideal mixing are critical in establishing complete mass transfer. The design of a high-efficiency extractor must therefore exclude all influences that interfere with these two requirements. Unfortunately, countercurrent flow and ideal mixing are irreconcilable in all column extractors. The only apparatus which can satisfy these conditions simultaneously and therefore achieve stage efficiencies close to 100% is the mixer-settler [15].

In mixer settlers, the two liquid phases are first mixed and then separated by settling. Either the light or heavy phase may be the phase dispersed in the mixing step, which is usually conducted in an agitated vessel. Agitation and residence time is sufficient to attain a reasonable approach to equilibrium (80% to 90% of a theoretical stage). The mixing device is generally an impeller. However, if dispersion is easily achieved and equilibrium is rapidly approached, as with liquids of low interfacial tension and viscosity, the mixing can be carried out by impingement in a jet mixer; by turbulence in a nozzle mixer, orifice mixer or other in-line mixing device; by shearing action if both phases are fed simultaneously into a centrifugal pump; or by injectors, where the flow of one liquid is induced by another.

The settling step is by gravity in a second vessel, the settler or decanter. Horizontal settlers commonly contain an impingement baffle to prevent the jet of the entering two-phase dispersion from disturbing the gravity-settling process. Vertical and inclined vessels may also be used. Emulsification in settlers is resolved by the implementation of various devices to speed settling. These include coalescers, separator membranes, meshes, electrostatic forces, ultrasound and chemical treatment. In cases where phase-density difference is small, the rate of settling can be speeded by employing centrifugal force.

Any number mixer-settler units may be connected to form a multistage, countercurrent cascade.

As complete phase separation is achieved at each step, backmixing is entirely eliminated in mixer-settlers. The favourable efficiency is retained even for large throughputs. These advantages account for the widespread use of mixer-settlers in industrial processes for many decades. However, mixer-settler equipment is complex. Each separation stage consists of a stirred vessel and settling vessel. In many cases, especially in early mixer-settler arrangements, the two phases have to be pumped between individual stages. Each settler needs an interface level control. Also, the horizontal arrangement results in a large area requirement [15].

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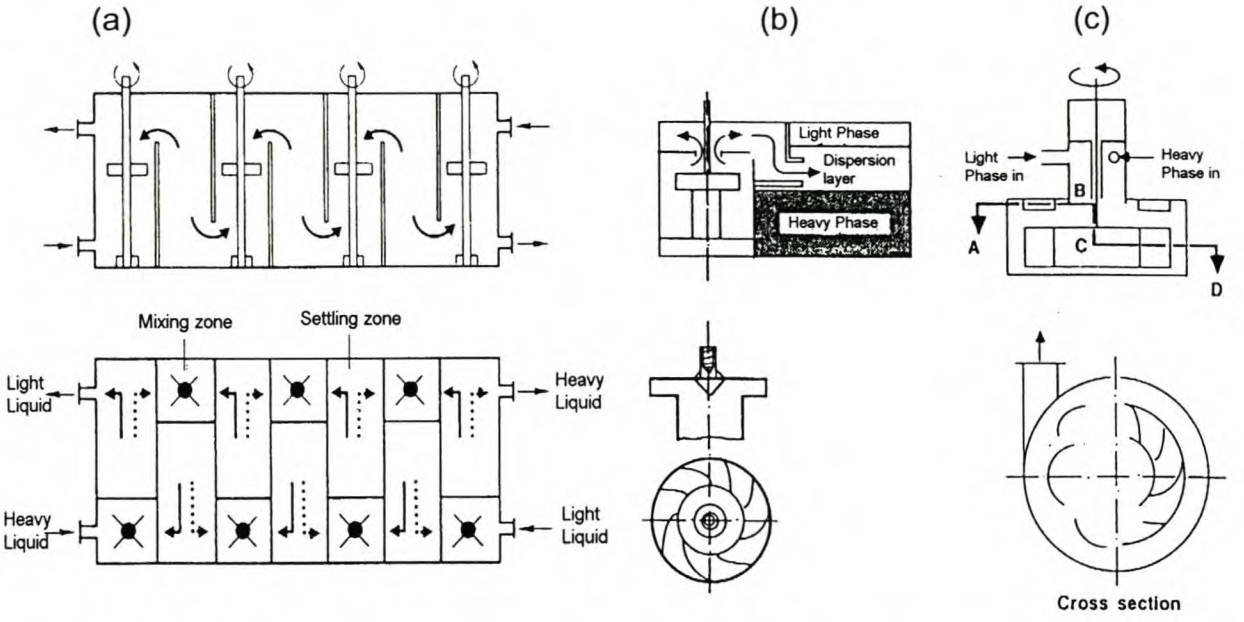

Figure 2.3-11: Mixer-settlers a) Box-type mixer-settler cascade [17]. **(b) Davy-McKee mixer-settler [20]; (c) IMI turbine pump-mix unit (cross-section A-B-C-D shown in lower part)** [15]

A number of different mixer-settler designs were developed to overcome these disadvantages, without foregoing any of the advantages. In the box-type mixer-settler (Figure 2.3-11a), the mixing and settling zones are combined in a single unit and are separated by an overflow weir for the light phase and an underflow slit for the heavy phase. The outlet of the settler acts as the inlet of the mixer. The agitator both disperses and moves the liquid phases. Unfortunately, the rate of rotation required to convey the light phase over the overflow weir may be too high in unstable systems and a high degree of entrainment may occur. As a result, mixing pumps with low shearing forces, and therefore low mixing intensity, have been developed. Examples include the Pumpmix impeller used in the Davy McKee mixer-settler (Figure 2.3-11b) [20] and the IMI turbine pump-mix unit (Figure 2.3-11c) [15].

The large area required by mixer-settlers arranged in horizontal configurations is overcome in the Lurgi extraction tower (Figure 2.3-12a), which was originally developed for extracting aromatics from hydrocarbon mixtures. In this tower, the phases are mixed by centrifugal mixers which are stacked vertically outside the column and driven by a single shaft. Settling takes place in the column and the flow of the two phases between the stages is guided by a complex baffle design located within the settling zones [9, 15].

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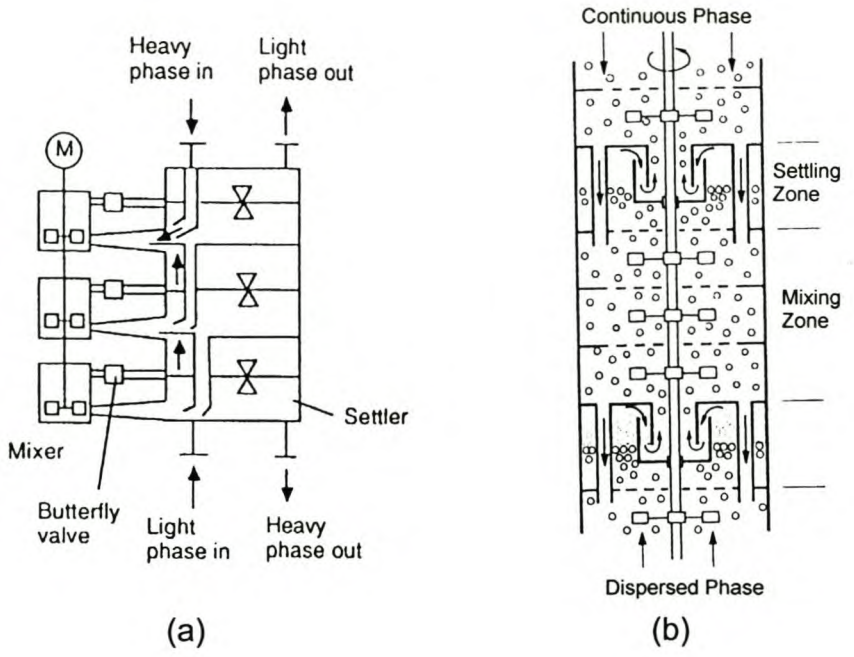

Figure 2.3-12: a) Lurgi extraction tower [9]**; b) Kühni mixer-settler column** [21]**.**

The Kühni mixer-settler column (Figure 2.3-12b) consists of a number of stages installed one on top of the other. Each stage is hydraulically separated and each has a mixing and settling zone. Mixing is by means of impellers identical to those used in the conventional Kühni extraction columns. The impellers do not need to transport the liquid phases from stage to stage. The rotational speed can thus be adjusted to achieve optimal droplet sizes. As the liquid phases are required to settle on every stage, the specific throughput achievable in a mixer-settler column is considerably lower than that achievable in similar extraction columns [21].

2.3.5 Selection of Extractors

Many of the extractors described have been used commercially in numerous industrial applications. The selection of an extractor for a liquid-liquid extraction process depends on many factors, the most important of which are throughput, fluid properties of the two liquid phases, number of theoretical stages required to achieve the desired separation and economic considerations.

Figure 2.3-13 gives a comparison of the capability of selected extractors with standard dimensions for the system toluene / acetone / water:

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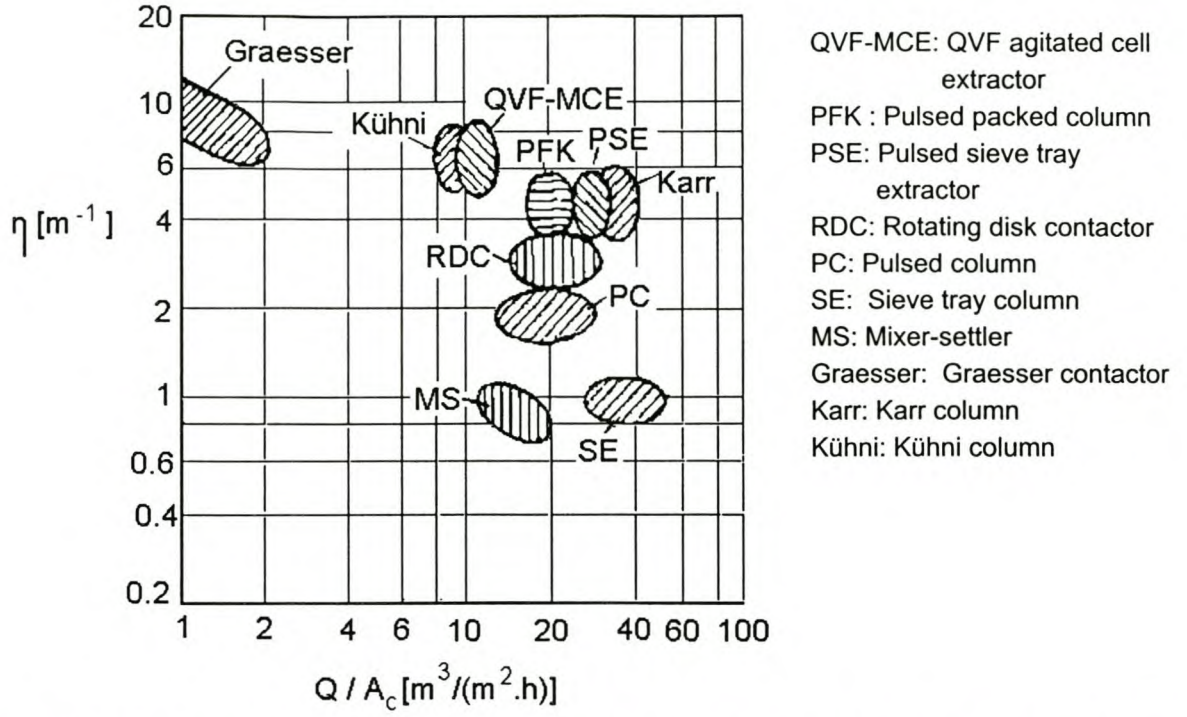

Figure 2.3-13: Number of stages per meter, η, of different extractor types as a function of the total volumetric throughput of the combined continuous and dispersed phases, Q, divided by cross-sectional area of column, A_c.

Representation according to Stichlmair [22] for the system Toluene / Acetone / Water. Volumetric flowrate ratio of dispersed to continuous phase is approximately 1.5.

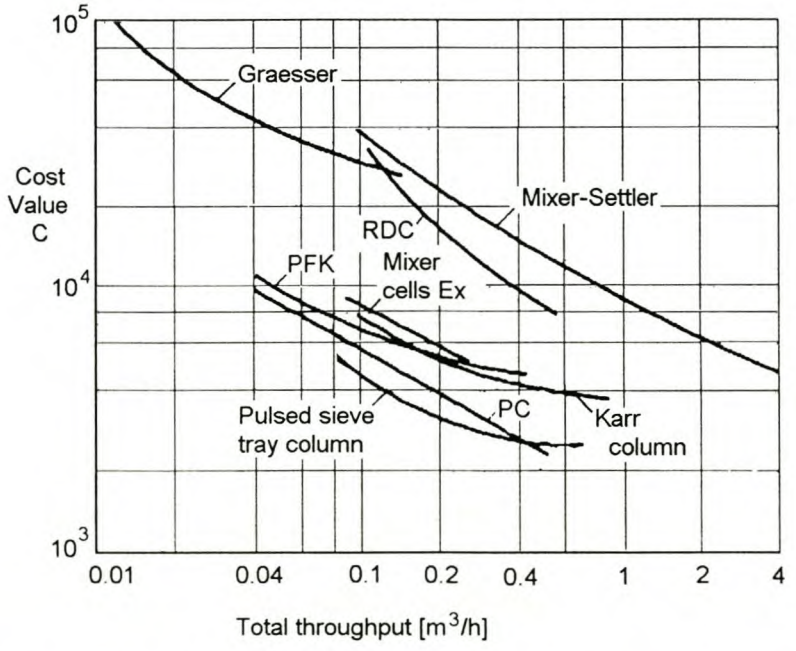

Figure 2.3-14 Cost value, *C*, as a function of the total throughput, for standard extractors where *C* = cost [$] / (throughput [$m^3$/h] x number of stages).

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Columns without mechanical agitation are the least expensive of the extractors available (see Figure 2.3-14). Initial costs as well as operating costs are low in comparison to agitated columns, centrifugal extractors and mixer-settlers. The main drawback of sieve-plate and packed columns is their low stage efficiency, making them suitable only for simple separations. Their applicability is also limited by their inability to handle high throughput and high flow ratios [15].

Columns with rotating internals are highly efficient extractors, but are constructionally more complex and therefore more expensive than unagitated and pulsed columns. They are therefore used only where a high degree of separation is required. While stage efficiency in an agitated column is not nearly that of a mixer-settler, a relatively large number of separation stages can be realised within a small overall height. The loading limit is generally lower than in pulsed columns, especially where density differences are small. Emulsifying systems cannot be handled.

Centrifugal contactors entail high initial costs, high operating costs and high maintenance cost. As such, they are generally used only in applications where other types of contactors are inapplicable, e.g. in systems where density differences are too small to achieve countercurrent flow in extractor columns.

Mixer-settlers are widely used due to advantages such as good contacting, high stage efficiency, low head-room, reliable scale-up, easy incorporation of many stages and ability to handle high throughputs and high flow ratios. Disadvantages such as large holdup, high investment and power costs, large floor space and the need for interstage pumping may make column extractors preferable.

It is commonly found that when new solvents are introduced, they have been used in novel types of extractor, which become a standard feature of the process. The rotating-disc contactor thus tends to be used with sulfolane, sieve-tray columns with the Udex process, and the Kühni column with DMSO. There are obvious advantages to the process developer and to the user if proprietary knowledge of the solvent is extended to the equipment. This is clearly demonstrated with sulfolane, where both solvent and extractor are Shell developments. Similarly, the NMP processes developed by Lurgi make use of their vertical multistage mixer-settler extractor [11].

In conclusion, the choice of extractor for a particular application depends largely on the characteristics of the liquid-liquid extraction system involved. The solvent selected for the application significantly influences these characteristics. Thus, a suitable solvent must first be selected for the separation of phenolic compounds from neutral oils. The characteristics of the proposed system must then be assessed, before a deciding on the type of extractor to be used. The capital and operating cost of the extractor must also be taken into consideration.

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2.4 Synergy of Liquid-liquid Extraction with Extractive Distillation

Extractive distillation and liquid-liquid extraction are both solvent-driven separation processes, i.e. separation between components in a homogenous feed mixture is facilitated by adding a mass-separation agent (MSA), or solvent [9].

The MSA can either be completely miscible with the feed mixture or it can be partially immiscible with one or more species in the mixture. In the first case, the second immiscible phase formed is a vapour phase. The key feed components split between the vapour and liquid phase and, in so doing, are separated. This separation may be enhanced if the MSA is used in conjunction with heat transfer, as it is in extractive distillation. In the second case, the second immiscible phase formed is a liquid phase consisting mainly of the MSA. In this case, the key components in the feed are distributed between the two liquid phases, i.e. separation is by means of liquid-liquid extraction [9]. While heat transfer may be incorporated in liquid-liquid extraction, it is usually not as critical to separation efficiency as it is in extractive distillation. In both cases, the MSA modifies the activity coefficients of the feed components in the liquid phase.

In both extractive distillation and liquid-liquid extraction, solvent selection is critical to the success of the process. In both processes the ease of separation and, therefore, the number of theoretical stages required, size and cost of the column, depends on the solvent. However, the criteria determining solvent suitability differ in the two processes.

In extractive distillation, a successful solvent is one that enhances separation by affecting the liquid-phase behaviour of each of the key feed components differently. It must be higher-boiling than the key components, should not form azeotropes with the other components and must be relatively non-volatile and thermally stable under the conditions in the columns [9].

In liquid-liquid extraction, a successful solvent is one that can exploit chemical differences in the feed components. Its boiling point can be either higher or lower than that of the feed components. Operating conditions in liquid-liquid extraction are typically less extreme than in extractive distillation. Solvent properties such as thermal stability and volatility are therefore not as critical in the initial solvent-based separation step, although they may well be critical in the solvent recovery step. This is an important distinction, as the operating conditions required for solvent recovery after liquid-liquid

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extraction may well be less severe than the operating conditions required for extractive distillation with the same solvent and same feed stream. Also, components that cause polymerisation of the solvent or react with the solvent at high temperatures may be removed, under relatively mild conditions, in the liquid-liquid extraction step. In the absence of these components, the solvent can be subjected to more extreme conditions during recovery, without polymerising or reacting. In the case of extractive distillation, the solvent would be subjected to relatively extreme conditions in the presence of all the feed components, including those that could cause polymerisation or reaction.

In these cases, the solvent may well be unsuitable for extractive distillation, but would be suitable for liquid-liquid extraction.

On the other hand, factors such as the difference in the solvent and feed densities as well as the solubility of the key components in the solvent are of paramount importance in liquid-liquid extraction, while being largely irrelevant in extractive distillation [23].

In both extractive distillation and liquid-liquid extraction, the destination of the feed components may be manipulated by the choice of solvent. I.e., depending on the solvent chosen, a particular feed component may be recovered in either the distillate or bottoms, in the case of extractive distillation, or in either the extract or raffinate, in the case of liquid-liquid extraction. This allows for flexibility in design in both solvent-based processes [23].

Both extractive distillation and solvent extraction require an extra separation step to recover the solvent from feed components. As such, both processes are considered only for separations which cannot be achieved by means of conventional distillation [23]. Liquid-liquid extraction processes often require two immiscible solvents to achieve separation. An extra solvent recovery column would thus be necessary. On the other hand, liquid-liquid extraction processes can typically handle larger fluctuations in feed compositions and feed streams with higher boiling ranges than can extractive distillation processes. A single extractor might thus be used for processing a particular feed stream by means of liquid-liquid extraction, where two or more extractive distillation columns, as well as a feed prefractionation column, would be required if the same feed stream was processed by means of extractive distillation.

Liquid-liquid extraction is often used in conjunction with extractive distillation throughout the petrochemical industry to separate azeotropic, pinched or close-boiling mixtures. Often, the same solvent may be used in either process to separate certain components. Factors such as the thermal stability of both the solvent and feed components, solvent losses and energy costs would then determine which process is used.

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2.5 State of the Art in Phenolic Recovery from Process Streams

As was discussed in Section 1.4., both aqueous and organic coal liquors are rich in phenolic compounds. The recovery of phenolic compounds from water, tars and organic hydrocarbons is therefore of particular interest in this study.

2.5.1 Recovery of Phenolic Compounds from Aqueous Streams

Phenolic-rich aqueous streams occur as condensate, byproduct and effluent streams of industrial operations such as gasification, coking, oil refining, foundries and resin manufacture. Phenolic compounds are toxic and, as a result, the removal thereof from these aqueous streams is an important field of research from an environmental as well as an economic point of view [24].

The removal of phenolic compounds by means of enzyme activity has been of increasing interest in recent years. Enzymes typically employed are laccase [25] and various peroxidases cultivated on plant material substrates such as soybeans[26], wheat bran [25] and plant root surfaces [27]. The peroxidases, either combined with a solvent such as polyethylene glycol or applied alone, polymerize phenolic compounds, thereby removing them from solution by precipitation. Removals in excess of 95% of the phenol, cresols, chorophenols and Bisphenol A encountered in selected industrial wastewater streams have been reported [26]. More than 97% of the phenol content of refinery effluent waters can similarly be removed by anaerobic wastewater treatment [28]. These processes are therefore very successful in removing phenolic compounds from aqueous media. They are however totally unsuited to the recovery of phenolic compounds as they necessarily result in the degradation or polymerisation of the phenolic compounds through enzyme activity [28], [25]. Biological treatments of phenolic-rich water are also severely impeded at high and fluctuating concentrations of phenolic compounds [29]. Aqueous streams with phenol concentrations as low as a few percent by weight cannot effectively be processed by bioremediation [30].

An alternative field of study which has been extensively investigated in the last decade is the removal of phenolic compounds from aqueous process streams by means of chemical oxidation with oxidising agents such as oxygen [31] and ozone [32], either with or without ultraviolet radiation or electrolysis [33]. As is the case with bioremediation of

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phenolic-rich waste streams with enzymes, oxidation processes result in the elimination of the phenolic hydroxyl group and will therefore not be discussed further.

A more applicable method for the removal of phenolic compounds from aqueous streams is adsorption. Phenolic compounds can readily be adsorbed onto a variety of adsorbent surfaces such as clays treated with surfactants [34], [35], lignite coal chars, granular activated carbon [36], fibrous activated carbon [37] as well as synthetic polymers and resins containing divinylbenzene copolymers [38]. The removal and recovery of the phenolic compounds from the various adsorbent surfaces is however very difficult, much more so than is the case with other organic compounds. This is especially true in the case of granular activated carbon [38]. In industrial processes, the phenolic compounds are typically desorbed from the activated carbons and synthetic polymer resins with a variety of different solvents such MIBK, acetone, DIPE, ethanol, benzene, toluene or methanol. Approximately 10 to 20% of the phenolic compounds cannot be recovered from the activated carbons and resins. The overall recovery of phenolic compounds from aqueous streams by means of adsorption is therefore seldom in excess of 85%. Also, as a residue of phenolic compounds remains on the activated carbons and resins, the adsorbent surfaces must be regenerated with hot oxidising gases. The conditions required for regeneration generally result in capacity losses of 5-15% [38], [39].

A novel method using liquid membranes for the recovery of phenolic compounds from aqueous streams has recently been proposed as an alternative [24]. In a liquid membrane the organic extractant phase is reduced to a thin liquid film which separates the feed liquid and stripping solution. Two configurations are typically implemented, namely Emulsion Liquid Membranes (ELM) and Supported Liquid Membranes (SLM). In ELM applications, the aqueous stripping and organic solvent phases form an emulsion which is suspended in the feed solution. In SLM applications, the organic solvent phase is adsorbed onto a microporous polymeric support, such as a hollow fibre, which separates the feed and stripping solutions. Supported liquid membranes with caustic stripping solutions are typically used for phenol recovery. In these applications the phenol diffuses from the aqueous feed stream through the organic liquid phase to react with the caustic stripping solution to give sodium phenolate. The effectiveness of the liquid membrane depends on the solubility and diffusivity of the phenolic compounds through the organic solvent phase. Polar solvents such as MIBK are therefore much better solvents for SLM recovery of phenols from water than non-polar hydrocarbons such as kersosene. However, the solubility of polar solvents in water may cause significant losses of extractant from the pores in the support matrix, which decreases the working lifetime of the liquid membrane. Another drawback of liquid membrane applications is that they cannot handle high solute concentrations in the feed solution. The optimum phenol feed concentration for a typical hollow fibre

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supported liquid membrane using a mixture of MIBK and kerosene as the organic solvent is approximately 2 g / L. [24]

The abovementioned processes are typically implemented for the processing of effluent water streams in which the concentration of phenolic compounds is low. Most industrial applications for the large-scale recovery of phenolic compounds from aqueous process streams are therefore based on solvent extraction and treatment with acids. Often, phenols from dilute aqueous streams are recovered as a more concentrated aqueous solution before being extracted with selective solvents. An example of such a process is the recovery of phenols from wastewater streams containing 0.5 to 4% phenol with sodium sulphate [30]. In this process the dilute aqueous phenol solution is distilled in the presence of 8 to 18% by weight sodium sulphate solution. The distillate separates into a water-rich and phenol-rich layer after cooling. The bulk of the sodium sulphate is recovered in the distillation bottoms product. The sodium sulphate in the water-rich layer of the distillate may be recovered by means of evaporative crystallisation. At least 60% of the phenol-rich distillate phase is made up of phenol, which may be recovered by means of solvent extraction [30].

The Lurgi Phenosolvan process is the most widely applied industrial process for the solvent extraction of phenolic compounds from aqueous process streams. A schematic diagram of the process as it is typically used in gasification, coke oven, coal hydrogenation and carbonisation plants is shown in Figure 2.5-1.

In the Phenosolvan process the filtered and cooled phenolic-rich aqueous feed stream is treated countercurrently with a suitable solvent, usually DIPE, in a multistage extractor. If large gas condensate feed flow rates must be handled, the extraction is performed in mixer-settlers. Lower feed flow rates can be treated in extraction columns, although many stages are usually required. The extract is separated by fractional distillation into a pure solvent (distillate) and crude phenolic product stream (bottoms product). The solvent is recycled to the extractor. The small amount of solvent contained in the raffinate is recovered by stripping with recycled gas. The solvent is then removed from the gas by absorption in the cooled and recycled crude phenol mixture. The solvent is subsequently removed from the phenol mixture in the stripping section of the fractionator [39].

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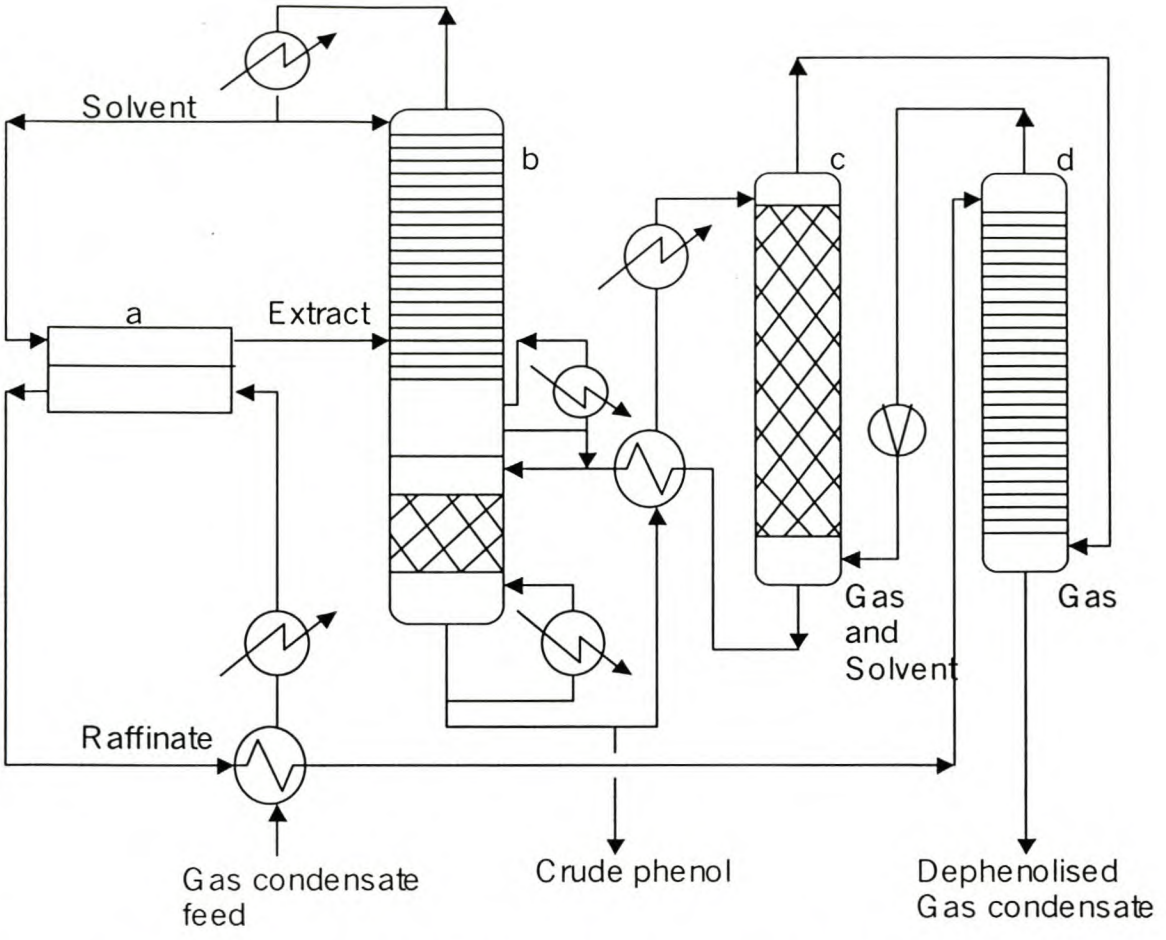

Figure 2.5-1. Lurgi Phenosolvan process for phenol recovery (with steam-saving solvent recovery by gas recycle) a) Extractor; b) Fractionator; c) Solvent Absorber; d) Solvent stripper [39].

The Phenosolvan process is a versatile process and can be applied successfully to a range of different aqueous feed streams, using different solvents or solvent mixtures, and various solvent recovery systems. Unfortunately, while the recovery of phenols is very high, a high percentage recovery of neutral oils is also obtained, i.e. the phenolic product must undergo post-purification to attain the required product purity of greater than 99% [39].

Alternative solvents to DIPE have been investigated for the extraction of phenolic compounds from aqueous streams. Countercurrent extraction processes with solvents such tricresyl phosphate, butyl acetate and benzene have been proposed prior to 1965 [40]. More recently, solvents such as cumene, alpha-methylstyrene [41] and MIBK have been investigated. In a comparison of DIPE and MIBK at temperatures in the range of 30 to 50°C, MIBK was found to be a more effective solvent for the extraction of phenols. MIBK is however more soluble in the aqueous stream than DIPE, leading to greater

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solvent losses. The recovery of MIBK from the phenolic product is by means of steam stripping, either at atmospheric pressure, or under vacuum [29].

Methyl-tertiary-butyl ether (MTBE) has also been proposed as an alternative solvent to DIPE and MIBK [42]. MTBE extracts phenol more effectively than DIPE and is less soluble in water than MIBK. After extraction with MTBE, the phenolics-ether extract can be separated either by distillation or by the use of an aqueous solution of an alkali metal hydroxide. In the latter process the phenols in the extract are converted to phenate salts which remain in the aqueous phase. The ether can then be removed by phase separation. After removal of the ether, the phenols in the aqueous phase may be liberated by treatment with carbon dioxide-rich flue gas. Residual ether dissolved in the aqueous phase can be removed by distillation. Alternatively, the solubility of the ether in the aqueous phase can be reduced by adding an aqueous alkali salt solution [42].

The capital cost of an activated carbon or resin plant is lower than that of a comparable solvent extraction plant. However, this advantage is negated by the high running costs for regeneration and replacement of adsorbents. Activated carbon and resin processes are therefore only economical for the treatment of dephenolised or biologically treated condensates and the treatment of small gas condensate flows. Large-scale recovery of phenolic compounds from aqueous streams with phenolic concentrations in excess of a few percent by weight is usually by means of solvent extraction [39].

2.5.2 Recovery of Phenolic Compounds from Coal Tar Iquors

While many processes have been implemented in industry for the recovery of phenolic compounds from aqueous streams, a commercially feasible process for the recovery of phenolic compounds from coal tar liquors has yet to be developed.

The classic process for recovering phenolic compounds from coal tar distillates is treatment with bases followed by acids and dates as far back as 1928 [1], [8].

In this process, the coal tar liquor is washed with a caustic soda solution. The phenolic compounds in the tar liquor react to produce sodium salts, while any other compounds present remain unreacted.

After 70-75% of the sodium hydroxide has reacted, the sodium salt solution is withdrawn and washed with a light neutral oil to remove any residual heavy neutral oils. Any neutral oils and pyridines remaining are then removed by steam distillation under vacuum. The cresylate solution is then treated with a carbon dioxide-rich flue gas in

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order to liberate the phenolic compounds. The resulting sodium carbonate solution is treated with lime to regenerate the caustic soda. Calcium carbonate is formed as a by-product of the process and is used in gypsum production.

The crude cresylic acid from the decanter after CO_2 treatment is dehydrated by distillation and fractionated into various isomers or mixtures of isomers. The final recovered phenolic mixture typically contains 45% phenol, 35% cresols, 15% xylenols and 5% other phenolic derivatives [1].

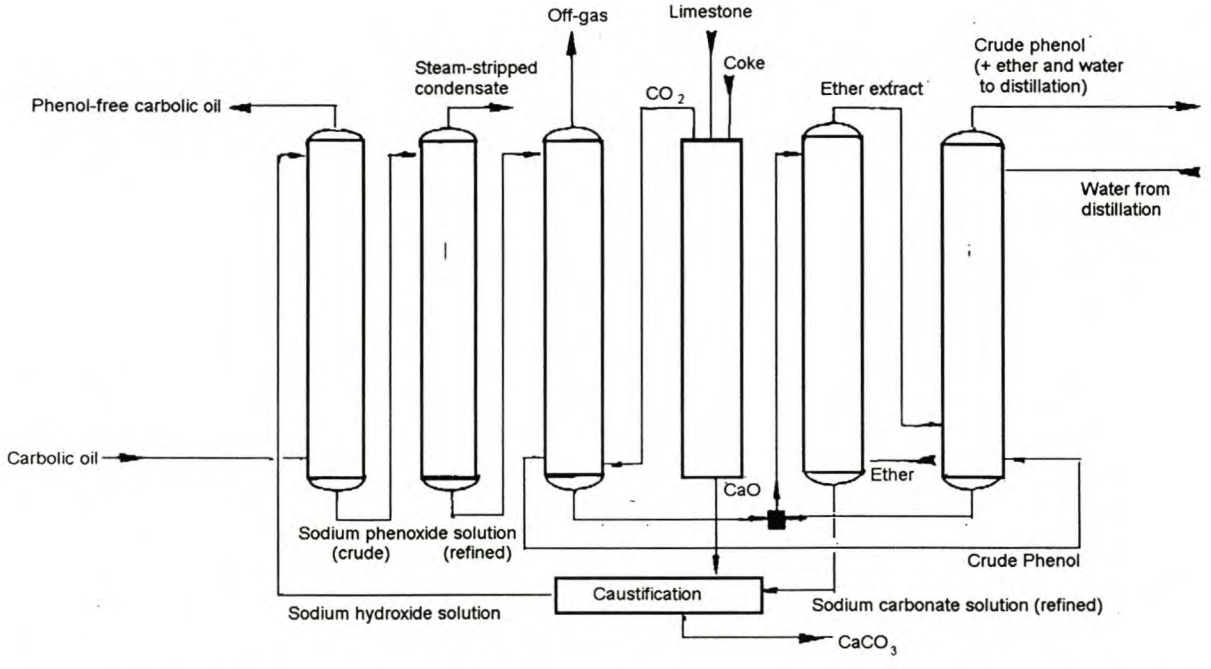

Figure 2.5-2: Isolation of phenols by means of treatment of sodium hydroxide [8].

This technology has some significant disadvantages. The concentration of the sodium hydroxide in the caustic soda solution must be many times in excess of the stoichiometric amount and even then a portion of the phenolic compounds remain unreacted and are lost with the neutral oils [8]. From a study carried out on the extraction of 2,4,6-trimethyl phenol from benzene with an excess of sodium hydroxide solution, it has been concluded that an increase in alkali concentration does not significantly increase the amount of the higher substituted phenols extracted from the organic phase. Also, the extraction of the 2,4,6-trimethyl phenol into the caustic solution decreases steadily as the process temperature is increased from 10 to 80°C. This is a serious problem as the extraction of phenolic compounds from tar liquors with sodium hydroxide solution must be carried out at elevated temperatures to prevent the crystallisation of naphthalene. As a result, a large proportion of the higher substituted

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phenols, especially those with methyl groups in the ortho position, remain in the tar liquor after treatment with the caustic soda solution [43].

A further disadvantage of the process is that it is energy-intensive and creates waste streams and materials which are difficult to remediate [8]. As a result, solvent extraction techniques have been investigated as an alternative means of achieving the desired separation.

Many of the numerous early solvent extraction techniques involved only a single solvent. Aqueous solutions of glycols [44], [45], [46], acetic acid [47], ethylamine, sodium salicylate [48], sodium phenate, methanol [49], [50], isobutyl acetate [51], n-butyl acetate [52], isoamyl acetate and isobutyl ketone [53] were employed. Solvent recovery was by means of distillation. The recoveries achieved with these processes were often very good, e.g. 95-96% recovery could be achieved with isobutyl acetate [51], but unfortunately all of these processes were incapable of achieving adequate phenolic product purity. Significant amounts of residual neutral oils and nitrogen bases remained, especially when phenolic recovery was high.

More recently, aqueous alkanolamines have been investigated as single selective solvents for the recovery of phenolic compounds from hydrocarbons. A coal liquor obtained from the hydrogenation of bituminous coal was fractionated and a light fraction (bp. <210°C) was extracted three times with 10% aqueous 2-ethanolamine. While the extraction of phenol was in excess of 90%, only partial extraction of the cresol isomers was obtained [54].

As single-solvent processes cannot yield high recoveries and high purities simultaneously, dual-solvent processes were investigated. These technologies usually involve a polar solvent to dissolve the phenolic compounds and a non-polar solvent to dissolve the neutral oil impurities. Polar solvents include methanol [46], ammonia [55], acetamide [56], acetic acid, ethanol [57], monoethylamine, sodium salts of sulphonic acids [7] etc. Non-polar solvents most commonly used are hexane, heptane, petroleum ether, diesel and various non-aromatic naphthas [49].

An example of the dual-solvent process is the aqueous acetamide - hexane process. While 90% of the phenolic compounds present in a low-temperature carbonisation tar oil may be recovered after two extraction steps, the extract has a very low purity of about 77%. It is therefore subjected to steam distillation and washing with a light aliphatic hydrocarbon, usually hexane. Significant amounts of the recovered phenolics are lost during these steps. During steam stripping, the acetamide is diluted, resulting in a decrease in phenolic solubility, and a subsequent loss of phenolics with the steam. The purity of the extract may be improved to above 94% with hexane washing, but the recovery is then reduced to about 80%. The phenolic compounds are finally recovered

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from the acetamide solution by dilution with water in order to reduce the phenolic solubility [56].

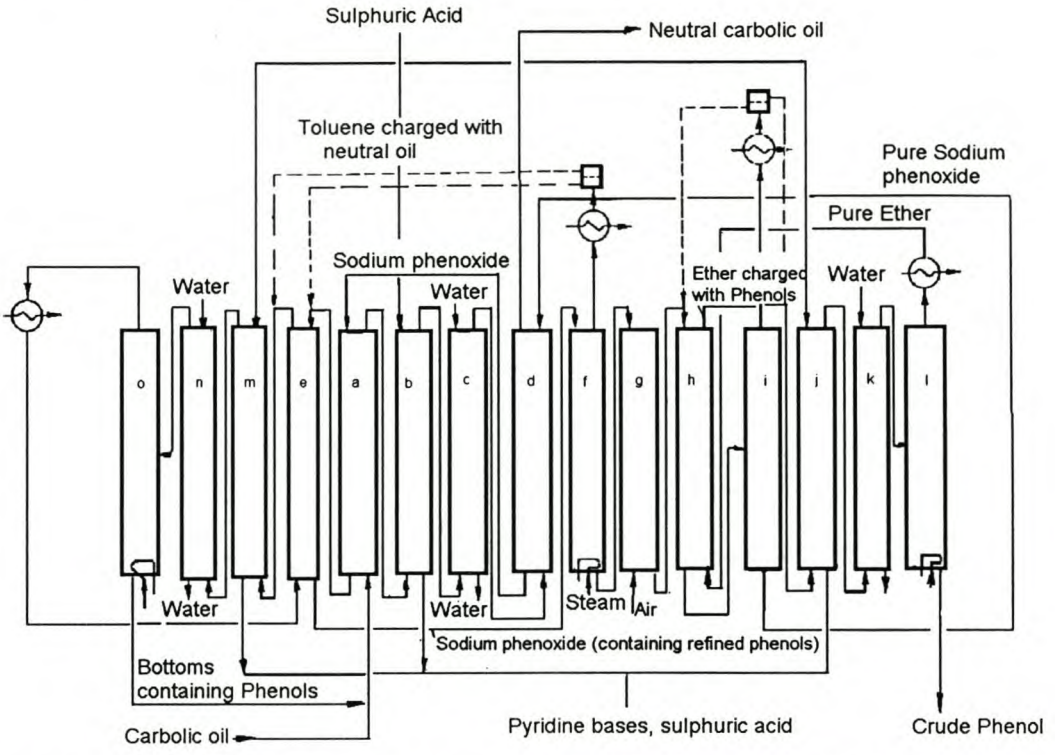

Figure 2.5-3. Flowsheet for Phenoraffin phenol isolation process [8].

a) Oil extraction with sodium phenoxide; b) Oil de-basing by extraction with sulphuric acid; c) Oil extraction with water (neutralisation); d) Oil extraction; e) Removal of phenols from sodium phenoxide solution; f) Steam stripping; g) Air blowing; h) Ether extraction of refined phenoxide solution of phenols; i) Ether stripping; j) Ether de-basing by extraction with sulphuric acid; k) Ether extraction with water (neutralisation); l) Separation of ether and crude phenol (distillation); m) Toluene de-basing by extraction with sulphuric acid; n) Toluene extraction with water (neutralisation); o) Toluene distillation.

The Lurgi Phenoraffin process (see Figure 2.5-3) is the only industrially important process in which crude phenol is extracted from coal liquors by selective solvents [8]. The solvent used in this process is aqueous sodium phenoxide, which has an excellent solvency for phenols. The coal liquor typically undergoes two countercurrent extraction steps with a phenoxide solution in which the molar ratio of unreacted phenol to sodium phenoxide can be as high as 3.5:1. Between steps, the coal liquor is de-based with dilute sulphuric acid. The phenolic compounds are extracted from the phenoxide solution extract by diisopropylether (DIPE). Hydrocarbons and pyridines are extracted from the supersaturated solution of phenols with a solvent such as toluene. After de-basing with dilute sulphuric acid and extraction with water, the toluene is regenerated

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with distillation. The distillation bottoms contains phenols and hydrocarbons and is recycled with the coal liquor. After the toluene extraction step, the phenoxide extract is steam-stripped in order to remove residual toluene. The phenols are then extracted with DIPE. The traces of DIPE dissolved in the phenoxide solution are removed by distillation. The ether phase, which contains phenoxide solution is de-based with sulphuric acid, washed with water and separated by distillation into DIPE and crude phenol. The DIPE is recycled and the phenol is purified by distillation. An obvious disadvantage of the Phenoraffin process is its complexity. A typical plant contains numerous distillation and extraction columns. Capital costs and operating costs are high.

A modification of the Phenoraffin process has more recently been investigated using a four-stage countercurrent extraction with a feed coal fraction with a boiling range of 140-220°C and a phenolic concentration of about 35%. The solvent used is a phenolate solution consisting of sodium hydroxide, phenol, cresols, 2,4- and 2,5-xylenol in water. The phenolics in the homogenised outlet aqueous phase are recovered by extraction with pure MIBK (methyl-isobutyl-ketone) followed by distillation. The process is however not viable as the final phenolic recovery is extremely low at 60.5% [58].

Another process that has found industrial application is countercurrent extraction with aqueous methanol and hexane (see Figure 2.5-4). In this process it is critical that the methanol in the aqueous solution is kept at 50-75% by weight. Methanol concentrations lower than 50% result in the formation of three liquid phases, while too-high methanol concentrations result in an increase in the solubility of the neutral oils in the solvent, resulting in poor product purity. Phenol and cresol recoveries are generally higher than 90% [59].

Drawbacks of this process include the high solvent ratios required and the correspondingly excessive recovery costs. Also, the purities of the phenolic products obtained in multistage countercurrent extraction are 97% at best. Impurities such as the nitrogen bases are very difficult to remove with this process - in fact aqueous methanol has been proposed as a solvent for the recovery of nitrogen compounds from coal liquors [60].

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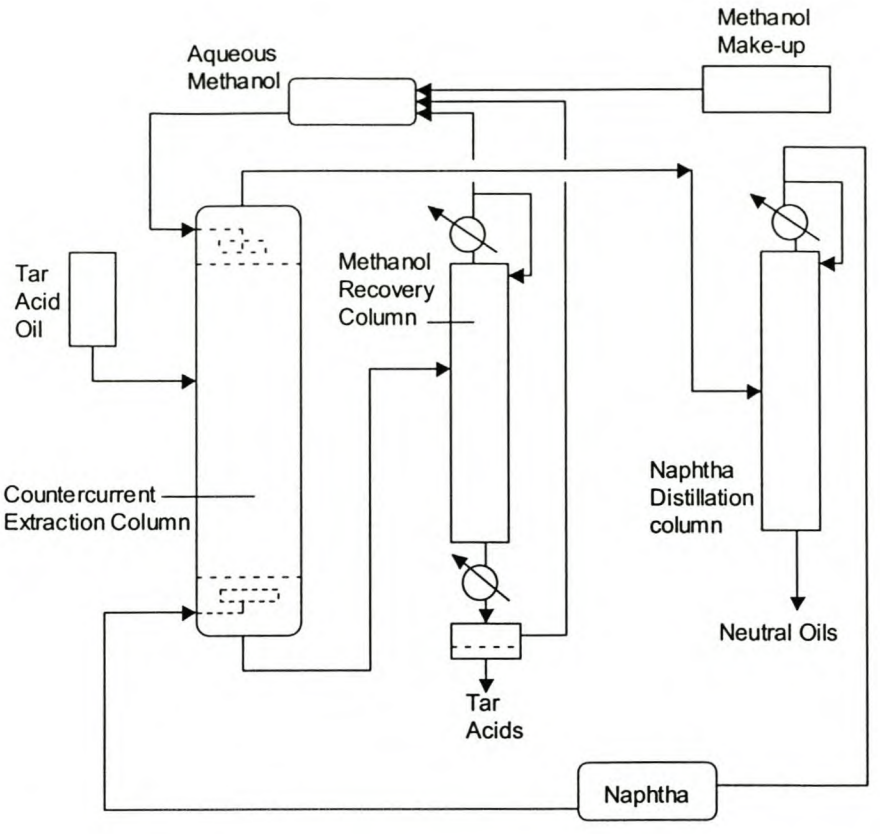

Figure 2.5-4: Aqueous Methanol - Hexane Liquid-liquid Extraction Process Flowsheet. Postpurification operations are not included [59].

Another drawback of the aqueous methanol method and indeed most methods using aqueous, light-boiling solvents is that after removal by distillation of the solvent, the bottoms product consists of two phases, namely an organic phenolic phase and a water phase. Decanting the water from the wet phenolic product is difficult. After decanting, the residual dissolved water must be distilled from the phenolic phase [7].

In an attempt to circumvent this problem, a dual solvent process using a mixture of triethylene glycol (TEG) and glycerol as a high-boiling solvent and hexane as a countersolvent was proposed and patented (priority date 28 May 1996) [7]. The percentage of glycerol in the solvent mixture is in the range of 65% to 75% for tar oil distillates and 85% for feed streams with a high phenol composition.

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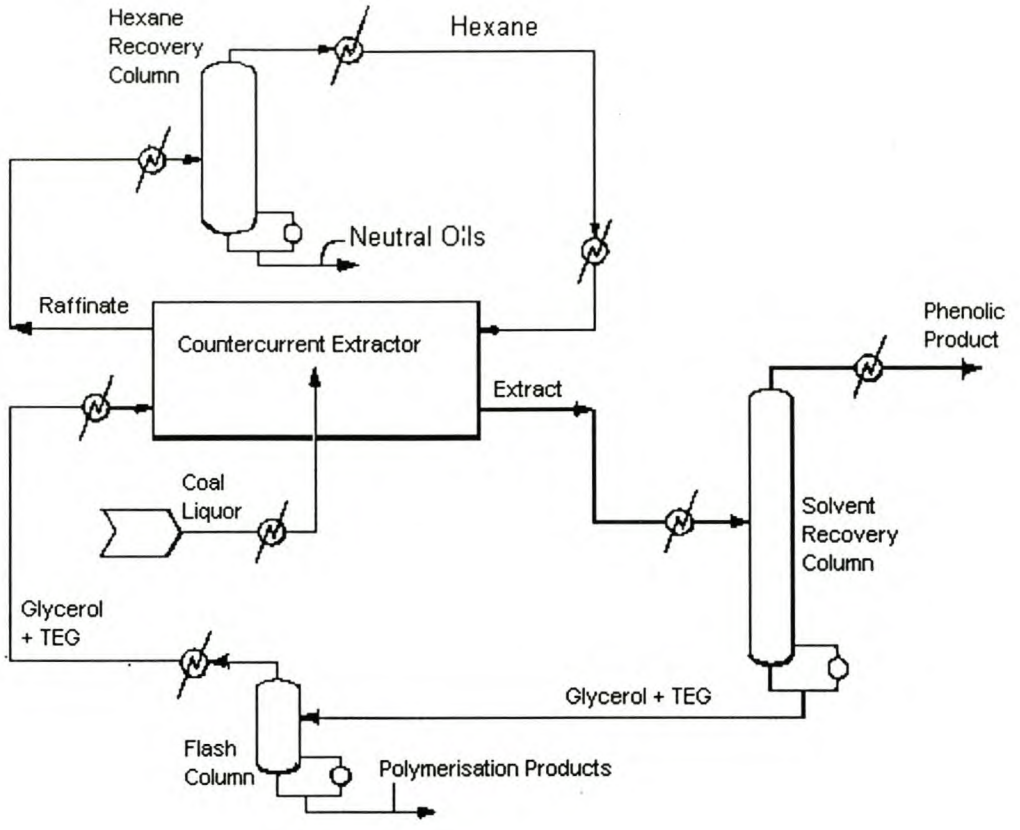

Figure 2.5-5. TEG-Glycerol Liquid-liquid Extraction Process Flowsheet. Postpurification operations are not included [7].

Extraction takes place in a counter-current mixer-settler arrangement (see Figure 2.5-5). The neutral oils are removed by the hexane phase and the phenolic compounds are extracted into the solvent phase. The hexane is distilled from the neutral oils and recycled. The extract phase is distilled and the phenolic compounds recovered as distillate. The high-boiling solvent mixture is then pumped to a flash distillation column or falling film evaporator in order to flash the solvent to separate it from polymeric materials which are formed in the reboiler of the solvent recovery column. A phenolic recovery of 92% is reported, with a total neutral oil weight percent of 1.37%. The nitrogen base content of the product is not reported. The product may then be treated with sulphuric acid to remove the residual nitrogen bases. Thus, after sulphuric acid treatment, the total neutral oil content of the phenolic product may be reduced to below 800 ppm [7].

The most significant disadvantage of the TEG-glycerol process is that the phenolic product must undergo postpurification to achieve the required purity of greater than 99.5%. Apart from the cost involved, the waste generated by sulphuric acid treatment is very difficult to handle and to remediate. Another important disadvantage is the high

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solvent ratios and solvent losses involved. A heavy solvent to tar ratio of 4:1 is required when treating tar distillates. As the entire high-boiling solvent volume must be flashed after solvent recovery, these high solvent ratios translate to high energy costs. In addition to this, hexane to feed ratios may be as high as 8:1. Solvent losses due to polymerisation of the solvent in the reboiler of the phenolic recovery column can be expected [7].

The high viscosity of the solvent mixture leads to additional complications. Solvent handling is difficult and the disengagement of the liquid phases in the extractor is slow. It is thus preferable that the extraction process is heated to 56°C to facilitate phase separation. Residence times are long. Also, up to ten theoretical stages are required. Taking all these factors into consideration, it is clear that column extractors are not suited to this process. Expensive mixer-settler arrangements would have to be employed to ensure thorough mixing of the two liquid phases [7].

TEG and glycerol have previously been investigated as solvents for single solvent systems for the recovery of phenolic compounds [44]. In the evaluation of the theoretical suitability of a mixture of triethylene glycol and glycerol for this application, the performance of the individual solvents in the single solvent extraction processes is of interest. Anhydrous triethylene glycol reportedly extracted almost all the phenolics from a tar oil fraction boiling up to 201°C in three theoretical counter-current stages. The solvent-free extract consisted of 82% phenolic compounds and 18% neutral oils. Dry glycerol extracted phenol very well from synthetic feed mixtures containing no other phenolic compounds. However, glycerol could not achieve a high selectivity or extraction efficiency when treating a phenolic mixture and commercial fractions [44].

This conclusion was confirmed in the investigation of a solvent system consisting of glycerol, water and hexane, using a synthetic feed stream consisting only of m-cresol and o-tolunitrile [61]. The m-cresol recoveries achieved with batch extractions were very low, typically in the range of 61-77%. The effect of the water concentration in the solvent phase had a negligible effect on these recoveries. However, increasing the hexane ratio to feed ratio from 3.0 to 5.0 led to significant decreases in the m-cresol recoveries.

As such, it is unlikely that a solvent mixture with a very high glycerol content will yield high phenolic recoveries from tar liquors in which the higher substituted phenols are prevalent, especially when used in conjunction with high hexane to feed ratios

A similar dual solvent process has also been investigated in which a distilled tar fraction is contacted with aqueous ethylene, diethylene or triethylene glycol, followed by washing of the extract with a light petroleum ether. In this investigation, it was concluded that 80% aqueous ethylene glycol was the optimum solvent with respect to

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phenolic recovery and product purity. The product purities obtained were however very low, with values ranging from 82-93% [62]. Also, the authors clearly overlooked the solvent recovery step since the boiling point of ethylene glycol (197°C) is virtually the same as the cresol isomers (~202°C). Their proposed ethylene glycol solvent system therefore simply cannot work.

Typical disadvantages of all the proposed solvent extraction processes for the recovery of phenolic compounds from coal tars are: the high solvent ratios required, high solvent losses, the complex postpurification required to achieve the desired phenolic product purity, the poor recovery of higher substituted phenols and the toxicity of the reagents used.

As an alternative to solvent extraction, the recovery of phenolics by means of extractive distillation with a polyhydric alcohol, such as a glycol, has been proposed and patented (priority date 28 May 1996 [49]). This process is illustrated in Figure 2.5-6. The phenolic compounds form hydrogen bonds with the polyhydric alcohols and their volatility decreases. The tar bases and neutral oils have a much smaller tendency towards hydrogen bonding and their volatility remains unaffected. The impurities may thus be removed as a distillate during extractive distillation. The phenols are removed with the solvent as a bottoms product and are subsequently recovered with distillation. The solvent is recycled.

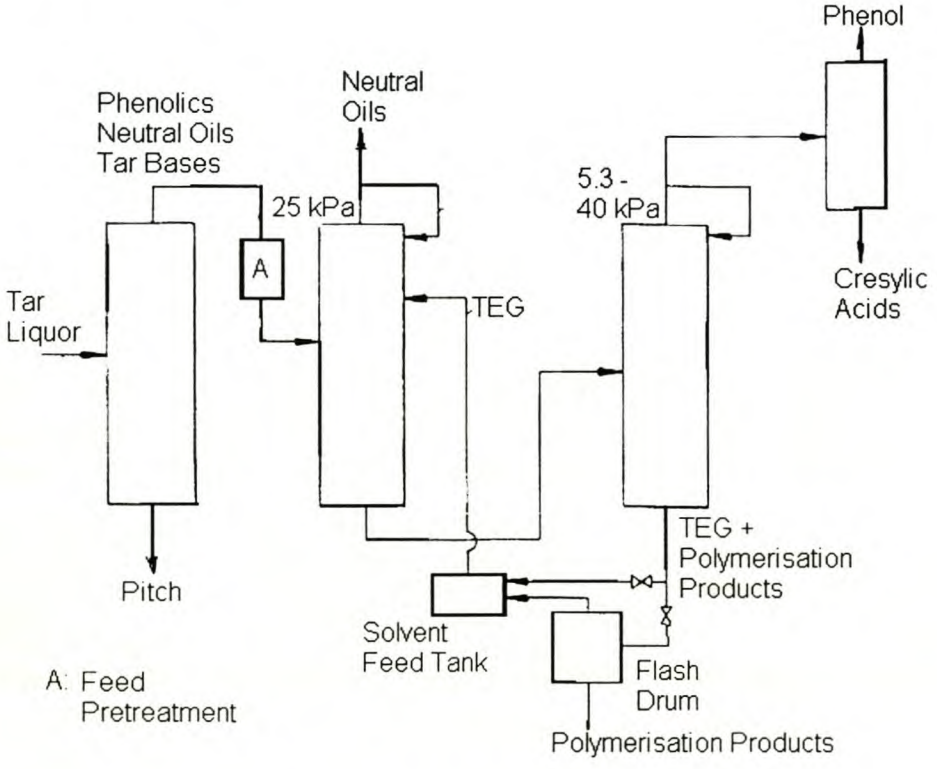

Figure 2.5-6: Flow diagram for TEG extractive distillation process [7].

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Unfortunately, extractive distillation is only effective for the purification of narrow boiling-range distillate fractions. Thus, middle coal distillates with wide-boiling ranges containing phenol, cresols, xylenols and ethylphenols would have to undergo fractionation prior to the extractive distillation step. In continuous operations, a separate extractive distillation train would be required for each narrow-boiling feed fraction.

Other disadvantages are inherent to the proposed extractive distillation process as a result of the high temperatures involved. The boiling points of the polyhydric alcohols, or glycols, are in excess of 200°C. Reboiler temperatures should however not exceed 220°C as the glycols are prone to thermal decomposition. Polymerisation may also occur in the reboiler at high temperatures, especially in the presence of the aromatic nitriles that commonly occur in coal tar distillates.

As such, liquid-liquid extraction is indicated as a more favourable approach to the separation problem, provided that a sufficiently selective solvent can be identified.

2.5.3 Post-purification of the Phenolic Product

None of the solvent extraction processes proposed to date for the extraction of phenolic compounds from coal tars yield a phenolic product with the desired purity of 99.0-99.5%. The phenolic product must therefore undergo post-purification in order to remove residual neutral oils and nitrogen bases. This is typically achieved through acid treatment followed by vacuum distillation, steam stripping or by means of strongly cationic resins.

The purification of phenolic mixtures of tar origin with acid treatment is a well-established practice [63], [64], [65]. Nitrogen bases such as ammonia, aniline, pyridine and its homologues are converted to their salts and the phenolic compounds can thus be separated from them by means of distillation. Phosphoric, hydrochloric, hydrobromic, benzene sulphonic and naphthalene sulphonic acids are all suitable for the application. However, the acid most commonly used is 0.5 to 5.0 weight percent 98% sulphuric acid [64]. After acid treatment the phenolic product undergoes vacuum distillation at temperatures lower than 140°C. The acid treatment and vacuum distillation may also be combined as a single process step. E.g. pyridines are removed from cresol mixtures by vacuum distillation at 80-150°C in the presence of sulphuric acid. The sulphuric acid to pyridine ratio is usually in the order of 2:1 by weight [63].

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Acid treatment is also typically implemented in the purification of phenolic mixtures obtained from aqueous process streams by means of the Phenosolvan process [39].

1-5% phthalic acid anhydride has recently been proposed as an alternative to sulphuric acid. The acid treatment is carried out at elevated temperatures and is followed by fractional distillation. The advantage of using phthalic acid is that sulphur compounds such as disulphide and mercaptans are simultaneously removed with the nitrogen bases. The purification process can further be improved through the addition of small amounts, 0.01 to 0.5%, of quinone. Treatment with quinone in the absence of the acid has no effect on the product purity. The crude phenol stream is mixed with the phthalic acid and, optionally, quinone for 5 to 30 hours at a temperature of 100 to 180°C. The mixture is then fractionally distilled under vacuum. The nitrogen and sulphur impurities remain in the distillation residue. The disadvantage of the process is the long retention time required for the reaction to complete and the relatively high operating temperature. As such it is only applied to phenolic mixtures that have significant residual sulphur concentrations [66].

Tar phenolic mixtures containing less than 1% water can also be purified of tar bases such as amines and pyridines by means of contacting with strongly acidic cation exchangers such as Amberlyst 15 [67], [68]. Concentrations of less than 1 ppm tar bases can be achieved after a contacting time of 30 minutes at ambient temperature [67]. Resins with gel structures, such as the Wafati and KPS resins may also be used to remove pyridine bases, but are ineffective for the removal of neutral oils [68].

Activated clay layers have also been proposed for the adsorption of nitrogen base impurities out of phenolic mixtures. While mixtures of phenols, cresols and xylenols with nitrogen base concentrations as low as 0.2 ppm may be obtained with this method, it has the drawback that the phenolic compounds must first be gasified at 250°C before passing through the clay layers [69].

Another novel process that has been proposed for the removal of nitrogen bases from phenol fractions obtained from tars, is thermal treatment with an isophorone (3,5,5-trimethyl-2-cyclohexen-1-one) solution. In this process the crude phenol mixture is either mixed with isophorone at a temperature of between 130 and 180°C before undergoing fractional distillation, or it is distilled in the presence of isophorone. The amines react with the ketone to form high-boiling compounds and can thus be separated from the phenolic compounds through distillation. A 57% reduction in the nitrogen base impurities remaining in a phenolic fraction recovered from coal hydrogenation tar can reportedly be obtained with a 1-5% isophorone solution [70].

While many processes are available and have been proven commercially for the removal of residual nitrogen bases and neutral oils from phenolic mixtures, it is clear

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from the above discussion that the post-purification of the crude phenolic mixtures is complex and therefore costly. As such, a recovery method that can yield a phenolic product which does not require post-purification will have a significant advantage over the existing recovery methods.

2.5.4 Separation of Individual Phenolic Isomers

Once the phenolic compounds have been recovered from the coal tar fractions, or formed by means of chemical synthesis, the individual phenolic isomers in the resulting mixture must be separated. This is usually done by means of dissociation extraction, a process that exploits the difference in dissociation constants, i.e. strengths as acids or bases, of the components in the mixture. Thus, in a mixture of m- and p-cresol, the stronger acid, m-cresol, reacts preferentially with a stoichiometric deficiency of an aqueous strong base to form a dissociated salt that is soluble in the aqueous phase. The weaker acid, p-cresol, remains undissociated and soluble in organic solvents. In a multistage countercurrent process, separated components of high purity may be achieved. The aqeuous phase is then acidified to free m-cresol. p-Cresol is distilled from the organic solvent.

In 1973, this dissociation process was modified to avoid the continuous consumption of strong base and acid. In the modified process, reagents which are only weakly acidic or basic are used. The mixture of cresol isomers may thus be contacted with an aqueous solution of trisodium ortho-phosphate, which is sufficiently basic for the separation to proceed as before. The aqueous phase leaving the contactor, containing the salt of the purified m-cresol, is then contacted with fresh organic solvent which has a high affinity for cresol. The weak dissociation is reversed, the m-cresol extracted by the solvent, and the regenerated phosphate salt is recycled. Finally the purified cresols are distilled from the organic solvents [10].

One of the most significant industrial processes for the separation of m- and p-cresol isomers at present is the Cresol Sorbex^{SM} process. This process utilises the Sorbex technology which was developed by UOP for the separation of a component or group of components from a mixture by selective continuous counterurrent, liquid-phase adsorpion on a solid adsorbent. In this process, a continuous countercurrent process in which fluids are contacted by a moving bed of solid adsorbent is simulated in a single extractor, without solids movement. This simulation is achieved by continuously moving the entry and withdrawal points of the cresol liquid mixture to and from the extractor by means of a single rotary valve. The Cresol Sorbex process can recover p-cresol at purities in excess of 99%. Recoveries in excess of 95% can simultaneously be achieved [71].

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2.6 Application of Glycols in Solvent Extraction Processes

It can be seen from the more recent patents discussed in Section 2.5.2. that the current trend in phenolic recovery processes is towards the use of various polyhydric alcohols as solvents in either extractive distillation or solvent extraction. Glycols in particular have long been considered as solvents for the separation of phenolic compounds from neutral oils and nitrogen bases. However, to date the proposed glycol solvent extraction and extractive distillation processes have been unsuccessful in achieving the required phenolic product purity. This could be attributed to the fact that the emphasis in the investigation of glycols has been on single solvent and two-step dual solvent extraction systems. Extraction processes in which the tar liquor feed stream is simultaneously contacted with a glycol-rich polar solvent phase and non-polar countersolvent phase have not been thoroughly investigated

Glycols are compounds containing two hydroxyl groups attached to separate carbon atoms in an aliphatic chain. Although glycols may contain heteroatoms, they mainly consist of carbon, hydrogen and oxygen. Polyglycols such as tri-, tetra- and polyethylene glycols are distinguished by intervening ether linkages on the hydrocarbon chain, as represented by the general formula $C_nH_{2n}O_x(OH)_2$ [72].

Ethylene glycols are used as solvents in a number of processes. The first major commercial application of the ethylene glycols was in the extraction of benzene, toluene and xylene (BTX) as described in Section 2.2.1.2.. Diethylene glycol (DEG) and triethylene glycol (TEG) were originally used in the Udex process for BTX extraction and tetraethylene glycol, which has a higher capacity for aromatics, was subsequently used in the Union Carbide process. While solvents such as sulfolane and NMP have largely replaced glycols in BTX extraction, it is nevertheless clear from the Udex and Union Carbide processes that glycols are effective solvents for the separation of aromatic compounds from aliphatics [10].

The largest application of glycols as extractive solvents is currently in the dehydration of natural gas and air streams. Glycols are hygroscopic and have very low vapour pressures. They are therefore ideal solvents for the absorption of water out of gas streams. Ethylene glycol [73], DEG [74], TEG [75] and mixtures thereof are extensively used in the drying of natural gas and refinery gas streams [75]. The dehydration capacity of the glycol solvents can further be improved by the addition of components such as potassium carboxylate and neopentylalcohol. The tendency of the glycols to absorb aliphatic and aromatic hydrocarbons is simultaneously reduced [76].

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Polyethylene glycol (PEG) and triethylene glycol (TEG) can also be used in packed-bed absorbers for the simultaneous purification and dehydration of process air effluent streams containing organic solvent vapours such as benzene and toluene [77].

As was mentioned in Section 2.5.2, aqueous glycols have been investigated as selective solvents for the extraction of phenolic compounds from coal tars. Ethylene glycol and diethylene glycol are unsuited for this application as solvent recovery from the phenolic compounds in the extract is not possible. In addition to the fact that the boiling points of ethylene and diethylene glycol (197°C and 242°C respectively) are very close to those of a range of phenolic compounds, ethylene glycol forms an azeotrope with the cresol isomers [2].

Tetra and polyethylene glycol can also not be considered for the extraction of phenolic compounds as they are prone to thermal decomposition at temperatures in excess of 200°C [78]. The phenolic compounds in the extract will typically be recovered from the solvent by means of distillation. As the boiling point of the majority of the phenolic compounds is in excess of 200°C and that of tetra- and polyethylene glycol is in excess of 300°C, reboiler temperatures in excess of 200°C will be unavoidable - even under vacuum - in the solvent recovery column. The only glycol suitable for the desired separation process is therefore triethylene glycol.

Triethylene glycol is completely miscible with polar solvents such as water, alcohols, glycol ethers and acetone and is insoluble in non-polar solvents such as benzene, hexane, toluene, dichloroethane, chloroform etc [74]. It would therefore be well suited as a selective solvent in a dual solvent process with a non-polar countersolvent and a polar co-solvent such as water. Fluctuations in the feed composition are highly unlikely to have a discernable effect on the maintenance of two immiscible liquid phases in such a solvent system. Furthermore, the low mutual solubility between triethylene glycol and typical non-polar countersolvents ensures that solvent losses are kept to a minimum.

As is discussed in Section 2.5.2., triethylene glycol has in fact been tested in a dual solvent process for the extraction of phenolic compounds from neutral oils and was found to be ineffective [62]. It was however not contacted with the feed and countersolvent simultaneously. Also, the countersolvent used was petroleum ether. A variety of other countersolvents are available and may well be more effective. The concentration of water in the solvent system was also not necessarily optimal for the desired separation. Triethylene glycol can therefore by no means be disregarded as a possible solvent for the desired separation.

From the literature surveyed, it is clear that a wide range of processes have been proposed for the recovery of phenolic compounds from process streams. Of these processes, liquid-liquid extraction is indicated as the most promising for the recovery of

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phenolic compounds from coal tar liquors which contain high concentrations of a range of phenolic compounds, neutral oils and nitrogen bases. It is also clear that single solvent systems and two-step dual solvent systems are unlikely to yield the desired phenolic product purity and recovery. Therefore, a dual solvent liquid-liquid extraction process in which the polar and non-polar solvents are simulataneously contacted with the feed stream will be selected, investigated and optimised in subsequent chapters.

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CHAPTER 3. SELECTION OF THE OPTIMUM COMMERCIALLY AVAILABLE SOLVENT

3.1 Factors Affecting Solvent Selection

The key to an effective liquid-liquid extraction process is the selection of a suitable solvent. Suitability is primarily based on the selectivity, capacity, recoverability, physical properties, toxicity, cost and availability of the solvent [10].

The selectivity of a solvent for the desired solute over other feed components is usually the most important consideration in solvent selection. High selectivity enables the desired product purity to be achieved in fewer separation stages and reduces or eliminates the need for costly postpurification.

The amount of solvent in circuit and, consequently, equipment size and solvent recovery costs, is largely determined by the capacity of the solvent for the desired solute. As such, capacity is often as important a criterion for solvent selection as selectivity. Unfortunately, a compromise between selectivity and capacity must usually be found, as most solvents with high capacity have low selectivity and vice versa [10].

Solvent recovery is often critical to the success of a process. The extraction process must thus be reversible in the sense that the solvent must be easily recoverable [10].

The solvency and solubility of a solvent is important in more than one respect. In order to prevent solvent losses, the solvent should not be soluble in the raffinate. There should be no tendency towards third phase formation [10].

Physical properties such as boiling point, interfacial tension, density, viscosity, melting point and thermal stability must also be considered when selecting a solvent. The boiling point should differ significantly from that of the extracted solute to facilitate solvent recovery by means of distillation. A reasonably high interfacial tension and good differential density between liquid phases promotes phase separation. Low viscosity promotes both mass transfer and phase separation and reduces the power input required. A melting point above ambient temperature is obviously undesirable as piping and equipment must then be heated to prevent solidification of the solvent. Thermal stability at operating temperatures is imperative as decomposition leads to solvent loss and impurities in extract [10].

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Ideally, the solvent should be cheap and available form more than one supplier. However, as the solvent is recycled in most applications, this factor is only critical if solvent losses are high. Toxicity, corrosiveness and flammability of solvent should also be taken into account [10].

3.2 Traditional Solvent Screening Methods

At present, solvents for liquid-liquid separation technologies are generally selected on the basis of database searches and heuristics.

3.2.1 Database Searches

There are many databases containing component physical properties that are relevant to solvent selection. Searching these databases can identify solvents with properties that are desirable for a given application. Unfortunately, most available databases contain only a few thousand components and are limited to pure component data only. A significant amount of equilibrium data is listed for binary systems and a limited amount for ternary systems. There is however very little data available for systems with more components. Also, databases necessarily contain only solvents that have previously been tested. Suitable untested solvents can thus not be identified [79].

3.2.2 Heuristic Solvent Selection

Heuristics involve the identification of functional groups or types of chemical components that are likely to form interactions that facilitate separation with key components in the feed [23].

3.2.2.1 Selection by Homologous Series

Homologues of the solute to be recovered from the feed are often selected as solvents. These homologues are as a rule selective for the solute in question, tend to form near ideal solutions and rarely form azeotropes. This method of solvent selection is most effective if the components that are to be separated do not contain similar functional groups [23]. Unfortunately, the addition of a homologue usually only affects a liquid-liquid phase split if the mutual solubility of the feed components was already low [79].

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3.2.2.2 Deviations from Raoult's Law

In both liquid-liquid extraction and extractive distillation, solvents are often selected to give a positive deviation from Raoult's Law with one feed component and a negative deviation with another. Various charts, such as the Robbins Chart, give an indication of how solutions might deviate from Raoult's Law. Unfortunately, many molecules contain more than one functional group. It is possible that these groups will fall under conflicting categories on the Robbins chart. Other methods must then be used to ascertain which group should take preference. Also, there is no indication as to the number of liquid phases that will form [23].

3.2.2.3 Hydrogen Bonding

The formation of hydrogen bonds between one of the feed components and the solvent can greatly enhance the selectivity of the solvent for that particular feed component. A number of charts indicating the formation of hydrogen bonds between functional groups are available [23]. These charts are subject to the same limitations as the Robbins chart.

3.2.2.4 Polarity Effects

Polarity effects contribute significantly to the formation of immiscible liquid phases and deviations from Raoult's law. Polarity can most effectively be used to select solvents when the difference in polarity between the components to be separated is significant. A solvent should either have a higher polarity than the more polar key component or a lower polarity than the least polar key component. The polarity of a molecule can be quantitatively evaluated on the basis of dipole and quadrupole moments [9]. Heuristic solvent selection based on polarity effects has the same disadvantages as solvent selection based on hydrogen bonding and deviations from Raoult's law.

It is clear that there is no guarantee that the solvent selected by means of database searches and heuristics is indeed the optimum solvent. Such a selection is mostly qualitative and based on a single solvent property. A more effective selection method that delivers quantitative results and is based on more than one solvent property is ideally required.

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3.3 Computer-Aided Molecular Design of Solvents

Computer-aided molecular design (CAMD) is a powerful method for solvent selection. In this method, more than one required property of a solvent may be specified and its structure is then calculated through the use of group contribution methods. Selected solvents may consequently be compared quantitatively [79].

A large number of interactive, combinatorial, knowledge-based and mathematical programming CAMD algorithms have previously been developed and are discussed elsewhere [79]. The disadvantages of these algorithms are that they either rely heavily on the knowledge of the user for their success, or they are computationally intensive and susceptible to local minima traps.

Therefore, a CAMD method using a genetic algorithm was used to assist in selecting a solvent for the separation of phenolic compounds from neutral oils and tar bases. The advantages of using a genetic algorithm are that it does not rely on user-interaction, retains the efficiency of mathematical programming and can perform well in difficult search spaces. Also, several desired properties can be specified in the goal function, i.e. solvent selection is not based on a single property [80].

3.3.1 Desigining solvents with GA

A genetic algorithm (GA) is an optimisation method based on the concept of natural selection. Various possible solutions for a problem are evaluated according to specified criteria, which are quantified in a fitness function. The fitness function may be defined in any form provided that better solutions to the problem have higher fitness values. The algorithm will attempt to find the solution with the highest fitness value [80].

The possible solutions are referred to as "chromosomes". Each GA chromosome is a linear combination of encoding units or "genes" [79].

In the case of solvent selection, the chromosomes are molecules that are to be evaluated as possible solvents. As all molecules are a combination of various functional groups, the genes that make up the chromosomes are predefined linear or non-linear combinations of various functional groups. During optimisation, the genes are linearly combined to form the chromosomes. I.e. various combinations of functional groups are combined to form molecules of varying complexity [80].

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The use of predefined genes prevents physically unfeasible and reactive combinations of functional groups. It also facilitates the creation of molecules more complex than a simple combination of functional groups. Aliphatic and aromatic molecules can be designed simultaneously and the length of chromosomes can be varied [80].

The following properties are emphasised and incorporated in the fitness function when evaluating a chromosome as a possible solvent:

1. the selectivity of the solvent for the desired solute over other feed components;
2. the recovery of the desired solute in the extract;
3. the solvent boiling point;
4. the solvent melting point;
5. the formation of two immiscible liquid phases.

These properties will be discussed briefly in more detail.

The selectivity of a solvent for solute A as opposed to B is measured by the separation factor β_{AB} which is analogous to relative volatility in distillation:

$$\beta_{AB} = K_A / K_B \qquad (3.3\text{-}1)$$

where K_A and K_B are the distribution coefficients of component A and B respectively and can be expressed as follows [12]:

$$K_A = x^{I}_A / x^{II}_A \qquad (3.3\text{-}2)$$

K_A : distribution coefficient of component A
x^{I}_A : equilibrium fraction of component A in the extract phase
x^{II}_A : equilibrium fraction of component A in the raffinate phase

The distribution coefficient can have a value marginally smaller or greater than one and the extraction will still be feasible, while the separation factor must either have a value greater or much smaller than one for the extraction to be feasible. The higher the values of the distribution coefficient and separation factor, the easier the extraction will be [12].

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The percentage recovery, R_A, of the desired solute in the extract is defined as:

$$R_A = m^{I}_A / (m^{I}_A + m^{II}_A) \times 100 \qquad (3.3\text{-}3)$$

m^{I}_A : equilibrium mass of component A in the extract phase
m^{II}_A : equilibrium mass of component A in the raffinate phase

The recovery should be as high as possible. The importance of considering the recovery of the desired solute in solvent selection must be emphasised. Solvents selected on the basis of selectivity alone might require extreme solvent to feed ratios in order to obtain a satisfactory recovery of the desired solute.

The boiling point of the solvent should differ significantly from that of the feed components in order to facilitate solvent recovery. The freezing point should be such that the solvent will not solidify at ambient temperature. Two immiscible liquid phases must form.

Group contribution models are used to estimate various relevant properties of possible solvent molecules. Thus, separation factors and recoveries may be estimated using the UNIFAC method [81], while Joback's methods [82] can be used to estimate boiling and freezing points. The number of liquid phases formed can be determined with a liquid-liquid flash calculation.

A fitness value can therefore be calculated for each estimated property that is relevant to solvent selection. The weighted mean of the fitness values for each property is taken as the overall fitness for the molecule [79].

In the first iteration of the GA, a fixed number of chromosomes are evaluated according to the specified fitness functions. These chromosomes form the first generation. The best 10% are carried over unchanged to the second generation. The rest of the second generation is an evolution of the first generation. Evolution of a specific chromosome is by means of point mutation, crossover, insertion and deletion. Point mutation is the random replacement of a one gene with another. Insertion, and deletion respectively refer to the random insertion or removal of a gene. Crossover involves two chromosomes, each of which is broken into two segments. A segment of each chromosome is switched with a segment of the other chromosome, thus creating two new chromosomes [79].

The new generation is evaluated and undergoes evolution to form the following generation. At the end of a specified number of generations, a list of the chromosomes with the highest fitness values is reported [80].

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3.3.2 Application to Phenolic problem

3.3.2.1 Identification of feed

The first step in solvent selection is the identification of the relevant feed components to be separated. To this end, a naphtha stream produced as a by-product of the pressure gasification of coal was qualitatively analysed using an HP5890 GC-MS. The most significant groups of components identified were:

- Phenolic compounds
- Neutral oils including:
    - Aromatic nitriles
    - Alkylsubstituted benzenes
    - Alkanes or paraffins
    - Alkylsubstituted indenes and indanes
    - Naphthalenes
- Nitrogen bases including:
    - Aromatic amines
    - Pyridines

The phenolic compounds, neutral oils and nitrogen bases account for approximately 50%, 47% and 3% respectively of the naphtha stream. An individual component breakdown cannot be disclosed due to confidentiality considerations.

The most prevalent phenolic compounds are phenol and the three cresol isomers. Significant amounts of the six xylenol isomers are present, especially 2,4-, 3,5- and 3,4-xylenol. Smaller amounts of various ethyl-, methylethyl- and propyl-phenol isomers were also identified.

The trimethylbenzene isomers, 1,2,3-trimethylbenzene, pseudocumene (1,2,4-trimethylbenzene) and mesitylene (1,3,5-trimethylbenzene) are the most significant alkylbenzenes present in the naphtha stream, while undecane and dodecane are the two paraffins present. Indene, indane and naphthalene are present in greater percentages than the derivatives thereof.

Various alkyl derivatives of pyridine, the most prevalent of which are the methylpyridine isomers, make up the greatest proportion of the nitrogen bases. Approximately 2% of the total feed mixture comprises of aromatic nitriles and amines. The former consists

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exclusively of benzonitrile and the methylbenzonitrile (tolunitrile) isomers, while the latter consists of benzenamine (aniline) and the methylbenzenamine (toluidine) isomers.

Specific pure components were selected to represent each type of chemical component in the industrial mixture. The selection was based on concentration in the mixture and availability of the pure component. In order to facilitate analysis, the selected components were further subdivided into three groups with narrow boiling ranges. Each group contains at least one phenolic compound, combined with the neutral oils and nitrogen bases that potentially present the most difficult separation. The three groups are presented in Table 3-1.

Table 3-1. Composition of Synthetic Feed Mixtures

Component	Mass Percentage [%]	Boiling Point [°C]	Purity [%]	Supplier
Phenol Feed Mixture				
Phenol	71.0	181.8	99.5	Riedel-de-Haen
Benzonitrile	6.7	191.0	98	Fluka
Aniline	6.7	184.4	99	Fluka
5-Et-2-me-Pyridine	6.7	178.0	98	Aldrich
Mesitylene	9.0	164.7	>97	Fluka
Cresol Feed Mixture				
m-Cresol	53.3	202.3	99	Riedel-de-Haen
o-Tolunitrile	6.7	205.1	>97	Fluka
o-Toluidine	6.7	200.3	98	Fluka
Indene	20.0	183.0	>95	Fluka
Pseudocumene	6.7	169.4	>97	Fluka
Undecane	6.7	195.0	>95	Fluka
Xylenol Feed Mixture				
2,4-Xylenol	13.3	210.9	98	Merck
3,5-Xylenol	6.7	221.7	98	Merck
3,4-Xylenol	6.7	226.5	98	Merck
Naphthalene	40.0	218.0	98	Aldrich
Dodecane	26.7	215.0	>95	Fluka
Indane	6.7	176.0	>95	Fluka

The phenol feed mixture was used as the basis for solvent selection.

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3.3.3 Problem Posed to the Genetic Algorithm

SolvGen, an implementation of the genetic algorithm discussed in Section 3.3.1. developed by Van Dyk [79], was used to identify likely solvents for the separation of phenol from benzonitrile, aniline, 5-et-2-me-pyridine and mesitylene. SolvGen uses a gene set consisting of 531 start / end genes and 368 middle genes. Each gene may consist of up to six types of UNIFAC groups and each chromosome may contain up to eight genes. The total solution space is thus of the order of 10^{20} molecules. Each generation contains 10 000 chromosomes and typically 10 generations are used to deliver the optimum solvent.

A countersolvent and co-solvent were specified as part of the solvent system. Hexane was specified as countersolvent because it is relatively inexpensive, readily available and has been proven to effectively extract neutral oils in previously investigated dual-solvent phenolic recovery processes [49], [7], [59], [62], [61]. Also, it has a boiling point (68°C) which ensures trivial recovery from the neutral oils in the raffinate.

Water was specified as co-solvent because it increases both the polarity of the solvent phase and the aromatics range of the solvent, i.e.the concentration of aromatics in the feed at which the second liquid phase in the extractor disappears. An increase in solvent polarity should decrease the solubility of the neutral oils in the solvent phase, effectively increasing the selectivity of the solvent. An increase in the aromatics range of the solvent facilitates the formation of two immiscible liquid phases. Also, water is immiscible with hexane and the addition thereof to the solvent increases the likelihood of a two-phase formation.

In applying SolvGen, the composition of the feed components was specified as shown in Table 3-1. The dry solvent to feed mass ratio was specified as being 3:1 and the hexane to feed ratio as 4:1. A water to dry solvent mass ratio of 0.3 was specified.

Benzonitrile and aniline are the components in the synthetic phenol feed mixture that are potentially the most difficult to separate from phenol. Ideally, all traces of these components should be removed from the extract during the initial liquid-liquid extraction step. Failing that, it is possible to remove traces of aniline from the phenolic product by means of strong acidic resins. Residual benzonitrile impurities cannot be as easily removed. As such, the removal of benzonitrile during extraction is of a higher priority than the removal of aniline. The selectivity of each possible solvent was therefore evaluated on the basis of phenol-benzonitrile separation factors. These separation factors were calculated using the modified UNIFAC equation [83].

The problem specification is summarised in Table 3-2.

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The permitted boiling range for the predicted solvents is very wide (50-350 °C) and overlaps the boiling range of the phenolic compounds and neutral oils. This is intentional, as it must first be established if high- or low-boiling solvents are more favourable.

Table 3-2. Specifications for Solvent Selection based on Phenol Feed Stream

System Molar Composition		Solvent Properties	
(1) Phenol	0.052	Min. Boiling Point	50 °C
(2) Benzonitrile	0.005	Max. Boiling Point	350°C
(3) Aniline	0.005	Max. Freezing Point	10 °C
(4) 5-Et-2-me-pyridine	0.004	Min. β_{12} value	25
(5) Mesitylene	0.005	**System Specifications**	
(6) Water	0.397	Temperature	40 °C
(7) Hexane	0.332	Number of liquid phases	2
(8) Solvent	0.200	Component in Extract Phase	Phenol

No minimum value was specified for the phenol recovery. This property was evaluated interactively. I.e. solvents were selected on the basis of selectivity, melting point, freezing point and the formation of a phase split. Both phenol recovery and solvent recovery were reported for the selected solvents and could thus be taken into consideration when comparing the selected solvents.

A list of the solvents selected with SolvGen is presented in Table 3-3.

Table 3-3. Preliminary solvents predicted by SolvGen over a wide boiling-range.

Solvent Functional Groups	$\beta_{Phenol-Benzonitrile}$	Boiling Point [°C]	Melting Point [°C]	R_{Phenol} [%]	$R_{Solvent}$ [%]
$(CH_3\text{-}O\text{-})(\text{-}CH_2\text{-})(\text{-}C\ CH_3\ OH)\text{-}(CH_3\text{-}O\text{-})$	30.8	175	-20	98.4	99.7
$(CH_3\text{-})(\text{-}CH\text{-}OH)\text{-}(\text{-}CH_2\text{-}O\text{-})(\ CH_3\text{-}O\text{-})$	36.8	200	-15	98.4	99.7
$(CH_3\text{-}O\text{-})(\text{-}CH_2\text{-}O\text{-})_2(\text{-}CH\text{-}OH)\text{-}(CH_3\text{-})$	33.0	200	-15	98.4	99.7
$(CH_3C{=}O)\text{-}(\text{-}CH_2\text{-})(\ \text{-}CH_2C{=}O)_2\text{-}(\text{-}CH_3)$	31.8	271	56	99.2	99.1
$(CH_3\text{-}(CH_2)_2\text{-})(\text{-}CH\text{-}OH)\text{-}(\text{-}CH{=}CH\text{-})(\text{-}CH_2\text{-})(\text{-}CH{=}CH_2)$	11.1	248	-32	98.6	99.2

It is important to note that although the boiling-points of certain of the predicted solvents are such that solvent recovery will be virtually impossible, the predictions do establish

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that high-boiling solvents (with high molecular weights) are more desirable than low-boiling solvents.

A second solvent search was thus implemented, with the temperature range for solvent boiling point specified as 250-350 °C. The predicted solvents are listed in Table 3-4.

Table 3-4. Final predicted high-boiling solvents

Solvent Functional Groups	$\beta_{Phenol-Benzonitrile}$	Boiling Point [°C]	Melting Point [°C]	R_{Phenol} [%]	$R_{Solvent}$ [%]
$(CH_3\text{-})(\text{-CH-OH } CH_3)\text{-}(\text{-}CH_2\text{-O-})_4(\ CH_3\text{-O-})$	38.9	310	81	99.1	99.7
$(OH\text{-}CH_2\text{-})(\text{-}CH_2\text{-O-})_5(CH_3\text{-O-})$	42.7	313	89	99.4	99.7
$(CH_3\text{-O-})(\text{-CH-OH})\text{-}(\text{-}CH_2\text{-O-})_4\text{-}(\ CH_3\text{-O-})$	48.4	313	74	99.1	99.7
$(CH_3\text{-O-})(\text{-CH-OH})\text{-}(\text{-}CH_2\text{-O-})_3(\text{-}CH_2\text{-})(\ CH_3\text{-O-})$	42.1	290	52	99.1	99.7
$(CH_3C{=}O)\text{-}(\text{-}CH_2\text{-})(\ \text{-}CH_2C{=}O)_2\text{-}(\text{-}CH_3)$	31.8	271	56	99.2	99.2
$(CH_3C{=}O)\text{-}(\text{-}CH_2\text{-})_2(\ \text{-}CH_2\text{-O-})(\text{-}CH_2C{=}O)\text{-}(\text{-}CH_3C{=}O)$	32.7	316	90	99.1	99.7
$(CH_3C{=}O)\text{-}(\text{-}CH_2\text{-})_2(\ \text{-}CH_2\text{-O-})_3(\text{-}CH_2C{=}O)\text{-}(\text{-}CH_3)$	30.3	330	96	99.1	99.7

From Table 3-3 and Table 3-4 it can be deduced that molecules containing ether, hydroxyl and carbonyl functional groups should be effective solvents.

3.4 Deficiencies of a Purely Theoretical Approach

Although the thermodynamics of multicomponent liquid-liquid equilibria (LLE) is, in principle, as straightforward as that of vapour-liquid equilibria (VLE), it is difficult to obtain an expression for the Gibbs excess energy which is accurate enough to give reliable results for liquid-liquid systems. LLE are extremely sensitive to small changes in activity coefficients - much more so than VLE. The impact of activity coefficients on VLE is offset by the much larger impact of the pure component vapour pressures. In LLE, the activity coefficients are dominant. Therefore, while good estimates of VLE may be made using only approximate activity coefficients for systems where the pure component vapour pressures are accurately known, in calculating LLE, small inaccuracies in activity coefficients can lead to serious errors [81].

There is always a measure of ambiguity present when LLE parameters are obtained from reduction of VLE data. Even in cases where the experimental data are very accurate, it is usually not possible to obtain a truly unique set of parameters. When multicomponent vapour-liquid equilibria are calculated, results are often not sensitive to

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which sets of binary parameters are chosen. However, when multicomponent liquid-liquid equilibria are calculated, results are extremely sensitive to the choice of binary parameters. Therefore, it is difficult to establish reliable ternary or higher LLE using only binary parameters obtained from binary LLE ad binary VLE data. For reliable results it is usually necessary to apply at least some multicomponent LLE data [81].

An added complication is that far less LLE than VLE data are available. Therefore, it is far more likely that binary interaction parameters will be missing in LLE systems than in VLE systems. In most thermodynamic modelling applications, missing LLE parameters are simply replaced with known VLE parameters. The predictions possible in LLE are thus commonly inferior to those possible in VLE [81].

The SolvGen algorithm investigates a search space of billions of components. There will thus unavoidably be many more missing LLE parameters than VLE parameters in this search space. The prediction of solvents for liquid-liquid extraction applications will consequently not be of the same standard of those for extractive distillation applications. However, while the algorithm should not be expected to predict specific solvents for liquid-liquid extraction, it should be capable of providing a fairly specific indication of which type of solvent should be used. The range of solvents predicted by SolvGen should also be much narrower than those predicted by heuristics, as the prediction is based on more than one desired solvent property and the interaction of the solvent with all components and functional groups in the mixture is investigated.

Simulation packages such as PRO-II are dependent on the same thermodynamic models as SolvGen and therefore suffer from the same lack of LLE binary interaction parameters. The solvents predicted by SolvGen may therefore not be evaluated on the basis of simulations alone. It is imperative that solvents predicted for liquid-liquid extraction be experimentally verified.

Another potential problem is that group contribution methods cannot predict the possible reactions between components. Therefore, it must be experimentally ascertained that a predicted solvent does not react with any of the feed components

3.5 Experimental Verification of Solvent Selection

The performance of solvents analogous to those predicted with SolvGen was investigated by means of batch extraction tests. These tests typically require small volumes of chemicals and unspecialised apparatus. They are consequently simple and relatively inexpensive. Besides demonstrating the extraction process, batch extraction

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tests may be used for the identification of potential problem areas. They are therefore usually the first step in investigating the feasibility of any proposed liquid-liquid extraction process.

3.5.1 Experimental Procedure

3.5.1.1 Materials

The purity of the feed components phenol, benzonitrile, aniline, 5-et-2-me-pyridine and mesitylene were as specified in Table 3-1. Analyical grade hexane, methanol and acetone were obtained from NT Laboratories. The water used was glass-distilled. Anhydrous triethylene glycol with a purity of 97% was supplied by Fluka. 1-Methoxy-2-propanol with a purity of 98%, triethylene glycol monomethyl ether with a purity of 95%, tetraethylene glycol dimethylether with a purity of 99+% and acetylacetone with a purity of 99+% were obtained from Sigma-Aldrich.

3.5.1.2 Apparatus

The batch extraction tests were carried out in standard 250 mL glass separating funnels. A set of five extractions could be carried out simultaneously. Isothermal conditions were maintained by placing the separating funnels in a thermostatically controlled stainless steel water bath. The temperature in of the circulated water in the bath was 40°C. A temperature of 40°C was selected as the system temperature as it is a convenient temperature to maintain under typical South African conditions. It is also far enough below the boiling point of hexane that excessive losses of hexane through evaporation can be avoided.

3.5.1.3 Procedure

Known masses, measured with a precision of 0.001g, of the solvent under investigation, water, hexane and each of the feed components were separately added to each separating funnel. The feed components were added separately because the synthetic feed was not completely homogenous and even distribution of the components between the funnels could not otherwise be guaranteed.

After addition of all the components, the separating funnels were sealed with insulation tape to prevent evaporation losses. They were then thoroughly shaken for

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approximately 30 seconds to facilitate mixing of the two liquid phases. The funnels were positioned in the water bath so that the levels of their contents were below the level of the water. The portion of the separating funnel that protruded above the water level was covered in aluminium foil to minimise heat losses.

The separating funnels remained in the water bath for a minimum of twenty-four hours. They were shaken for approximately 10 seconds at four-hour intervals for the first twelve hours and then left to stand for at least another twelve hours before sampling.

Upon removal from the water bath first the solvent phase and then the hexane phase was separately drained from each separating funnel into glass bottles with screw caps. The outside of the separating funnels were dried prior to sample-taking to prevent contamination of the samples by any water adhering to the funnel. The entire sampling process was carried out immediately after removal from the water bath to ensure that the composition of the phases did not alter as the temperature dropped to ambient temperature. Each phase was weighed with a precision of 0.001g and diluted to prevent secondary phase formation. The last ~2 mL of the solvent phase and first ~5 mL of the hexane phase were individually drained into separate containers in order to prevent mutual interface contamination of the solvent and hexane bulk samples. The masses of these interface volumes were measured and incorporated into the total phase masses.

3.5.1.4 Analysis

The compositions of each of the resulting batch extraction phases were determined with a Hewlett-Packard 5890A gas chromatograph (GC) with a flame ionisation (FID) detector. Integration was performed with computerized integration software. A 60 m Zebron D68H5 capillary column (inner diameter 0.25 mm) was used. Response factors were determined using solutions of known concentrations. Toluene was used as an internal standard for the calculation of the concentration of hexane, mesitylene and volatile solvents. m-Cresol was used as an internal standard for the calculation of phenol, benzonitrile, aniline, 5-et-2-me-pyridine and heavy solvents.

3.5.2 Comparison of Solvents

Methanol was not predicted as a solvent by SolvGen. It has however been implemented industrially in a dual solvent phenolic recovery process, with hexane as countersolvent and water as co-solvent [59]. An indication of the efficiency of the predicted solvents can thus be obtained by comparing their performance to that of methanol.

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Unfortunately, the optimum water ratios for the published methanol extraction system are much higher than the water ratios used in the prediction of the high molecular weight solvents [59]. The aqueous methanol solvent must contain at least 50% by weight water in order to maintain two liquid phases. This is not the case with the predicted solvents. A comparison between methanol and the predicted solvents at identical water ratios is thus meaningless. The performance of methanol is therefore evaluated on the basis of a single batch extraction at the optimum solvent ratios for the methanol system. The performances of the predicted heavy solvents are evaluated on the basis of a series of batch extractions at various solvent to feed, water to solvent and hexane to feed ratios. The ranges over which these solvent ratios were varied are approximately the same for all the predicted solvents.

The comparison is thus biased in favour of methanol as the average performance of the predicted solvents is compared to the optimal methanol performance.

The performances of the predicted solvents as regards selectivity and phenol recovery are summarised in Table 3-5. The corresponding equilibrium compositions of the resulting liquid phases are listed in Appendix A1.

It is clear from Table 3-5 that, in terms of selectivity for phenol over both mesitylene and the nitrogen bases present in the feed, triethylene glycol is the most effective solvent tested. It is also clear that the separation of phenol from mesitylene should be trivial using any of the solvents tested. The phenol-benzonitrile, and phenol-5-et-2-me-pyridine separation factors are excellent, and good phenol-aniline separation factors can be obtained.

The phenol recoveries achieved with the solvents triethylene glycol, TEG monomethylether and tetraglyme are extremely good. TEG monomethylether yields a marginally higher phenol recovery than triethylene glycol. The difference can however be considered negligible as the phenol recoveries are so high. As a result, based on the significantly higher separation factors achieved with triethylene glycol, it can be concluded that triethylene glycol is the optimum commercially available solvent.

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Table 3-5: Separation factors, β_{ij}, percentage phenol recoveries, R_{Phenol}, and percentage aniline remaining in extract, $R_{Aniline}$, achieved with selected commercially available solvents at various solvent ratios.

Exp. ID.	m_{Solent} / m_{Feed}	m_{Hexane}/ m_{Feed}	m_{Water} / $m_{Solvent}$	R_{Phenol} [%]	$R_{Aniline}$ [%]	$\beta_{phenol-mesitylene}$	$\beta_{phenol-aniline}$	$\beta_{phenol-benzontirile}$	$\beta_{phenol-et-me-pyridine}$
Solvent = Methanol									
me1e	1.0	4.0	1.0	89.2	82.5	283.6	1.8	5.3	9.7
Solvent = 1-Methoxy-2-propanol									
mp1 c	1.0	3.0	0.1	70.9	67.3	11.0	1.2	1.8	2.2
mp2 c	1.0	3.0	0.3	88.2	83.1	55.8	1.5	3.1	4.7
mp3 a	1.0	3.0	0.7	90.2	85.5	109.5	1.6	4.2	6.9
mp3 b	1.0	3.0	1.0	Three liquid phases formed					
mp3 e	1.0	5.0	1.0	Three liquid phases formed					
mp1 a	2.0	3.1	0.1	77.2	75.7	7.2	1.1	1.5	2.3
mp1 b	2.1	2.9	0.3	90.7	86.4	53.0	1.5	3.2	4.9
mp2 b	2.0	3.1	0.7	91.9	86.2	143.9	1.8	4.8	8.2
mp3 d	2.0	3.0	1.0	88.9	86.8	107.6	1.2	4.3	8.0
mp1 d	3.0	3.0	0.1	84.2	82.0	7.1	1.2	1.6	2.0
mp1 e	3.0	3.0	0.3	92.4	89.1	58.3	1.5	3.3	5.3
Solvent = Triethylene glycol									
4C	2.0	3.0	0.7	93.5	86.1	679.0	2.3	10.2	27.1
6C	2.0	3.0	0.1	95.9	88.6	217.0	3.0	10.9	19.5
9C	2.0	3.1	0.3	95.6	88.3	672.0	2.9	11.3	22.8
1A	1.0	3.0	0.3	93.9	85.6	341.0	2.6	9.2	17.5
2D	1.0	3.0	0.7	92.3	82.7	371.4	2.5	9.3	18.7
6B	1.0	3.0	0.1	94.6	87.1	202.6	2.6	8.2	14.5
7D	3.0	5.0	0.7	93.9	83.2	624.5	3.1	16.2	33.8
6D	3.0	3.0	0.1	97.8	93.1	331.0	3.3	14.2	26.3
9D	3.0	3.0	0.3	97.1	91.6	716.4	3.1	14.5	29.6
Solvent = Triethylene glycol monomethylether									
e1a	1.9	2.9	0.3	97.4	92.6	437.4	3.0	12.1	22.7
e1b	2.0	3.1	0.7	96.5	90.4	636.4	2.9	12.4	23.8
e1c	1.0	3.0	0.3	95.7	89.0	297.1	2.8	9.0	15.5
e2a	3.0	3.0	0.3	97.3	93.6	398.5	2.4	8.7	21.6
e2c	3.0	3.0	0.1	98.4	96.3	243.2	2.4	9.6	23.1
e3a	1.0	2.9	0.2	95.9	89.4	203.7	2.8	9.1	15.4
e3c	1.0	2.9	0.7	94.1	87.7	326.3	2.2	8.1	16.0
e5b	1.0	5.0	0.3	94.0	84.4	286.6	2.9	10.0	17.9
e5d	1.0	5.0	0.7	91.4	81.6	513.5	2.4	9.9	14.7
Solvent = Tetraethylene glycol dimethylether (Tetraglyme)									
tg1a	1.0	3.0	0.3	94.8	88.6	146.8	2.3	6.1	11.6
tg1b	2.0	3.0	0.3	95.3	90.9	138.4	2.0	5.6	12.0
tg1c	3.0	2.9	0.3	96.0	93.1	147.8	1.8	5.8	12.4
tg1d	2.5	5.0	0.3	92.8	87.2	139.3	1.9	5.4	11.7
tg1e	2.5	4.9	0.5	93.6	87.2	237.3	2.2	7.2	15.2
Solvent = Acetone → Reacts with aniline in feed									
Solvent = Acetylacetone → Reacts with aniline in feed									

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CHAPTER 4. DEVELOPMENT OF AN IMPROVED SOLVENT

4.1 Effect of Functional Groups on Solvent Performance

While triethylene glycol is clearly a very effective solvent for the separation of phenol from neutral oils and nitrogen bases, an understanding of the effect of various functional groups on solvent performance could assist in designing a still more effective solvent.

The effect of functional groups on solvent performance is summarised in Table 4-1.

Table 4-1: Performances of commercially available solvents based on average phenol-nitrogen base separation factors, β_{ij}, phenol recovery R_{Phenol}, and aniline recovery, $R_{Aniline}$.

Solvent	Functional Groups	$\beta_{Phenol-Benzonitrile}$	$\beta_{Phenol-Aniline}$	$\beta_{Phenol-Etmepyridine}$	R_{Phenol} [%]	$R_{Aniline}$ [%]
Methanol	-C-OH (1)	5.3	1.8	9.7	89.2	82.5
Methoxy-2-propanol	-C-OH (1) -C-O-C (1)	3.1	1.4	4.9	86.1	82.4
Triethylene glycol (TEG)	-C-OH (2) -C-O-C (2)	11.6	2.8	23.3	95.0	87.4
TEG monomethylether	-C-OH (1) -C-O-C (3)	9.9	2.6	14.7	95.6	89.5
Tetraglyme	-C-O-C (5)	6.0	2.0	12.6	94.5	89.4
Acetone	-C=O (1)	Reacts with Aniline in Feed				
Acetyl acetone	-C=O (2)	Reacts with Aniline in Feed				

Molecules containing carbonyl groups are clearly not suitable solvents for the treatment of any feed stream containing primary amines, as the carbonyl groups react with the primary amine group. This leads to solvent losses and the contamination of the extract with the reaction products. Carbonyl groups may be considered for feed streams that do not contain primary amines.

From Table 3-5 and Table 4-1 it can be deduced that hydroxyl groups significantly increase the selectivity of high-molecular weight solvent molecules such as triethylene glycol, TEG monomethylether and tetraglyme. The phenol-benzonitrile, phenol-aniline and phenol-5-et-2-me-pyridine separation factors achieved with triethylene glycol (two hydroxyl groups) are each significantly better than those achieved by TEG monomethylether (one hydroxyl group) which are in turn better than those achieved with tetraglyme (no hydroxyl groups).

The effect of hydroxyl and ether groups on phenolic recovery is more complex. The results obtained with methoxy-2-propanol, triethylene glycol and TEG monomethylether

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indicate that phenol recovery increases with an increase in the number of ether groups in the solvent molecule. On the other hand, tetraglyme, which has five ether groups, yields a lower phenol recovery than triethylene glycol and TEG monomethylether, which have two and three ether groups respectively.

This discrepancy is caused by the effect of the solvent hydroxyl groups on phenolic recovery. The characteristic hydroxyl groups of the phenol molecules form hydrogen bonds with the hydroxyl groups of the solvent molecules. These hydrogen bonds hold the phenol molecules in the solvent phase and prevent them from dissolving into the hexane phase. Thus, additional hydroxyl groups in the solvent molecule can be expected to enhance the recovery of phenol.

The fact that TEG monomethylether yields a higher phenol recovery than triethylene glycol for all solvent ratios tested appears to contradict this hypothesis. This apparent contradiction can be attributed to the relative sizes of the phenol molecule and the solvent molecules. The phenol molecule contains an aromatic ring and is therefore fairly large in comparison to the straight chain solvent molecules investigated. Certain solvent molecules may simply be too small to accommodate more than one phenol molecule, resulting in a lower phenol recovery. Also, the hydroxyl groups in a solvent molecule may be too closely spaced on the molecule backbone to enable hydrogen-bond formation with more than one of them. I.e. the first phenol molecule to form a hydrogen bond with one of the solvent hydroxyl groups may shield the other closely spaced hydroxyl groups from other phenol molecules.

The inclusion of ether groups in the solvent molecule allows more space within the molecule matrix to accommodate the large phenol molecules. If the ether groups are correctly positioned, the distance between the hydroxyl functional groups on the solvent molecule backbone is also greater, which allows easier access by the phenolic molecules and consequently facilitates hydrogen-bonding.

Alkyl groups could arguably perform the same function as the ether groups. However, the solubility in hexane of a solvent molecule containing alkyl groups would be higher than that of an analogous molecule containing ether groups. Solvent losses would consequently be greater and a higher water content would be required to maintain two liquid phases. Another advantage of the ether groups over the alkyl groups is that they have the potential for forming weak associations with phenol molecules.

The balance between ether and hydroxyl groups is however not a simple numerical one. Methoxy-2-propanol has one hydroxyl and one ether group, while triethylene glycol has two of each. I.e. the ratio of hydroxyl to ether groups in the two molecules is the same. Yet triethylene glycol has a much higher phenol recovery than methoxy-2-propanol.

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The arrangement of the functional groups within the molecule, as well as the size of the molecule, must therefore play a role in phenolic recovery.

This is best illustrated in Figure 4.1-1, which shows the optimised spatial configurations of the molecules under consideration. Each molecule was individually optimised using ACD / ChemSketch (© Advanced Chemistry Development, Toronto, Canada). Optimisation is based on modified molecular mechanics which take bond stretching, angle bending, internal rotation and van der Waals non-bonded interactions into account.

Methanol and glycerol molecules are illustrated along with the predicted commercial solvents and phenol molecules. As was mentioned in Section 2.5, the m-cresol recoveries obtained with glycerol are not very good. Figure 4.1-1 clearly illustrates that the glycerol molecule is incapable of accommodating more than one phenolic molecule at one time, despite the fact that it contains three hydroxyl groups. It is also apparent that the shape of the methoxy-2-propanol molecule is not favourable for the accommodation of a large phenolic molecule.

As was mentioned in Section 3.3, the most difficult separation in the phenol feed stream is that of phenol from aniline. The highest phenol-aniline separation factors are achieved with triethylene glycol and, even so, their average value is only 2.8 in comparison to 11.6 for the corresponding average phenol-benzonitrile value (Table 4-1). While aniline can be removed in post-purification, it is preferable that it be reduced to acceptable limits during the extraction process.

Therefore, a final factor to be taken into consideration when evaluating the effect of the various functional groups on solvent performance is the effect of the hydroxyl groups on phenol-aniline separation. The difficulty of this separation is largely due to the fact that primary and secondary amines tend to form hydrogen bonds. The solvent hydroxyl groups therefore have a similar effect on the amine group of the aniline molecule as they have on the hydroxyl group of the phenol molecule. Nitrogen is however not as electronegative as oxygen. The N-H-O hydrogen bond is therefore not as strong as the analogous O-H-O bond [84]. This is reflected in the phenol and aniline recoveries shown in Table 3-5 and Table 4-1. Without exception, for all the solvents tested, the percentage of feed aniline remaining in the extract phase is lower than the corresponding phenol percentage. It should therefore be possible to optimise the ratio of hydroxyl and ether functional groups so as to achieve the maximum phenol recovery without retaining too much aniline.

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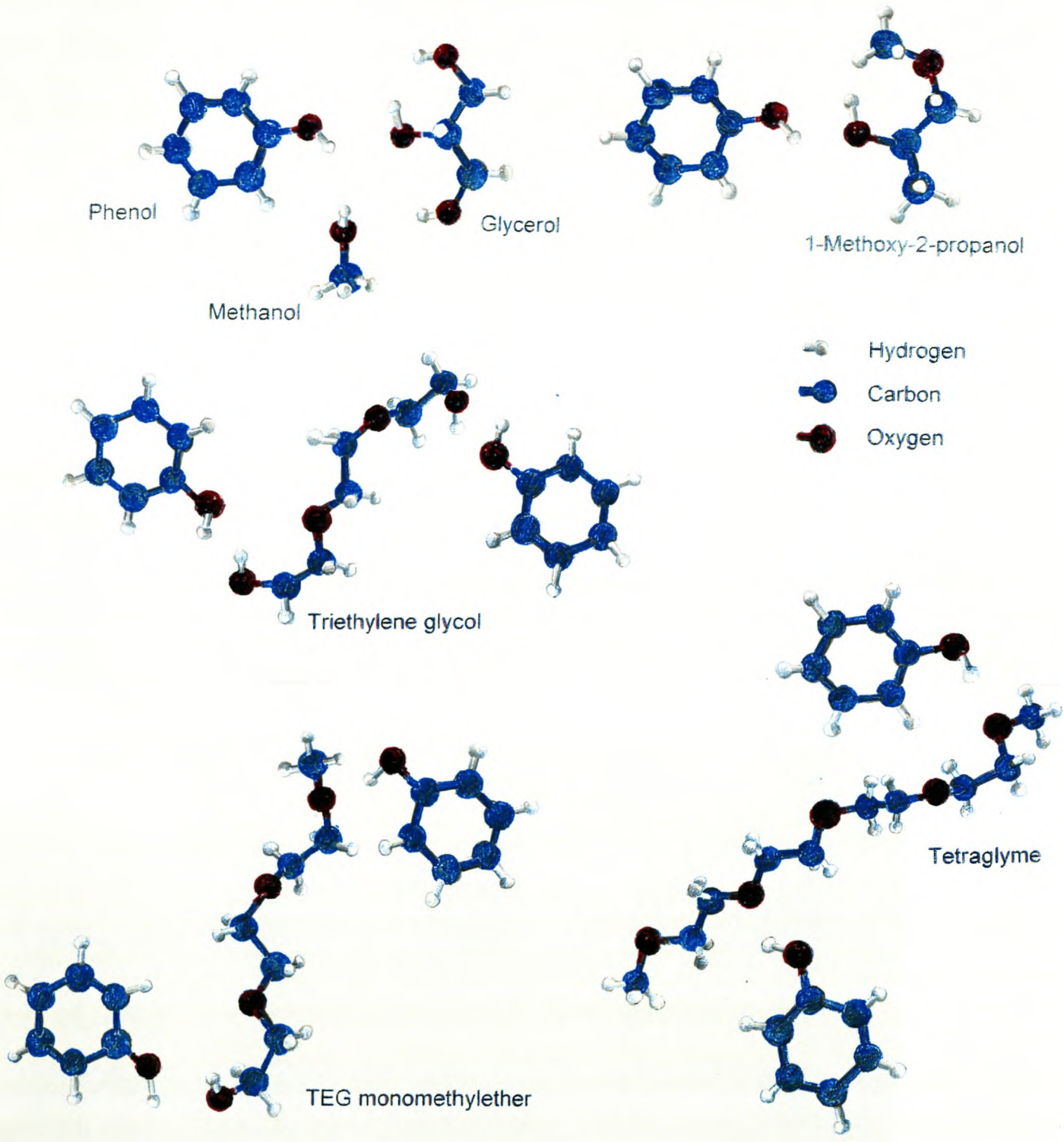

Figure 4.1-1.: Three-dimensionally optimised molecule structures for predicted solvents

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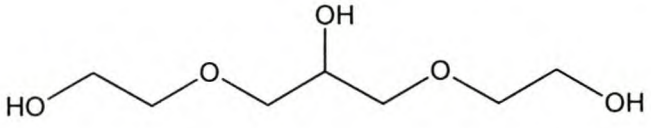
This is illustrated in the performances of triethylene glycol and TEG monomethylether. The recovery of both aniline and phenol is higher with TEG monomethylether. The additional phenol recovery achieved with TEG monomethylether in comparison to that achieved with triethylene glycol (95.6% as opposed to 95.0%) is however smaller than the additional aniline recovery (89.5% as opposed to 87.4%). As a result, the phenol-aniline separation factor is lower for TEG monomethylether than for triethylene glycol.

While triethylene glycol is a very effective solvent for the separation of phenolic compounds from neutral oils and tar bases, improved results should be possible if a solvent with a more favourable hydroxyl to ether functional group ratio can be found, provided that the hydroxyl groups are favourably spaced over the molecule backbone.

4.2 Predicted Optimum Solvent Structure

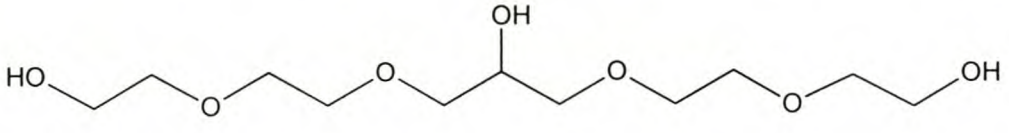
Two modifications of the triethylene glycol molecule are proposed as improved solvents. In the first modified molecule, 1,3-(ethoxy-2-hydroxy)-propane-2-ol, an additional -CH-OH functional group is inserted in the centre of the triethylene glycol molecule:



1,3-(ethoxy-2-hydroxy)-propane-2-ol,

The additional hydroxyl group is expected to increase the potential of the molecule to form hydrogen bonds.

However, as can be seen from Figure 4.2-1, the distance between hydroxyl groups is still not large enough to allow phenolic molecules unhindered access to all three groups. Therefore, a second modified solvent in which an additional $-CH_2-CH_2-O-$ group is inserted between each pair of adjacent hydroxyl groups, is proposed as an improved solvent:



1,3-(diethoxy-4-hydroxy)-propane-2-ol

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As can be seen in Figure 4.2-1, the hydroxyl and ether group arrangement in the extended molecule, 1,3-(diethoxy-4-hydroxy)-propane-2-ol, should be most favourable for phenol recovery.

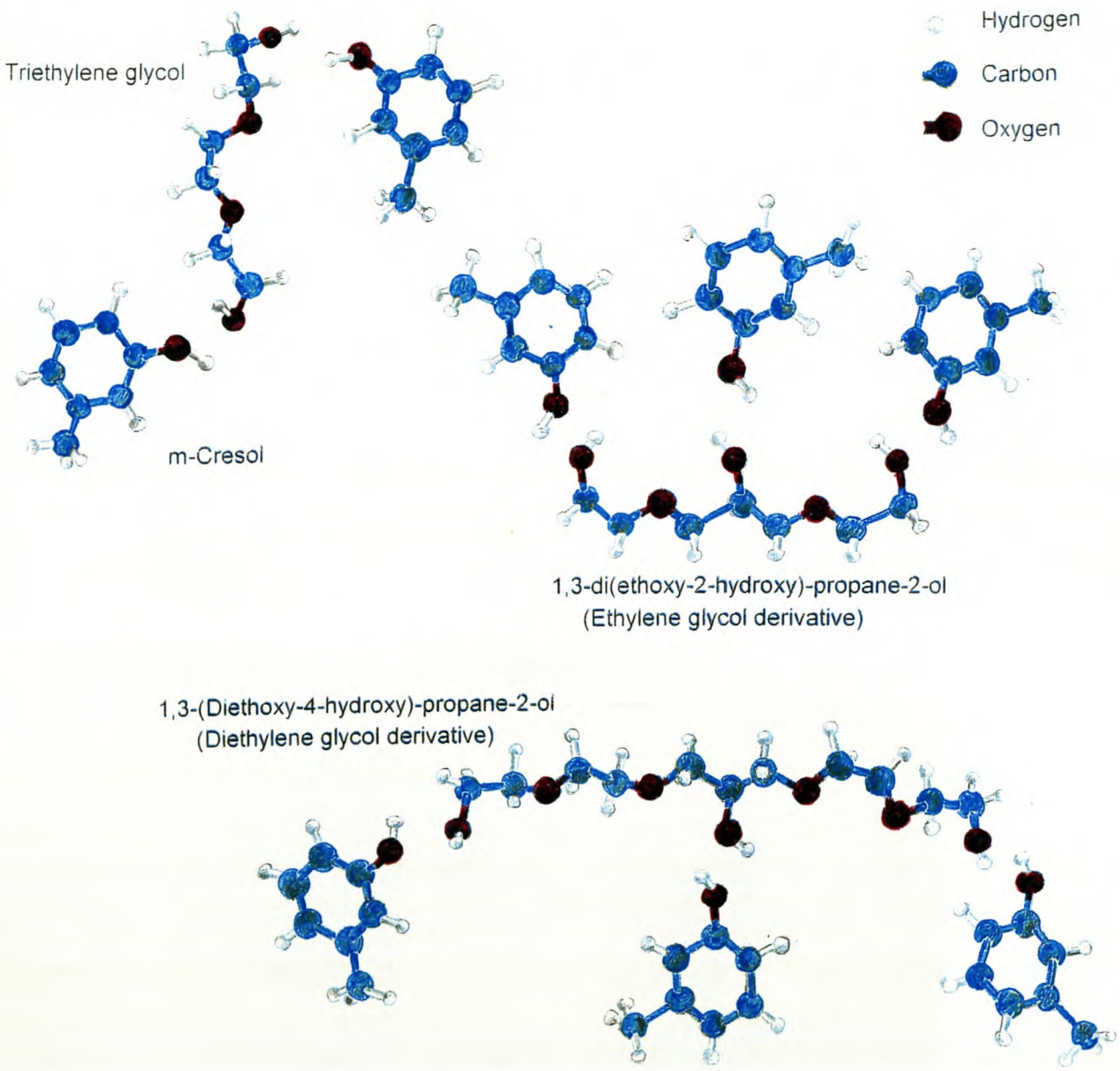

Figure 4.2-1 Three-dimensionally optimised molecule structures for triethylene glycol and synthesised solvents.

Unfortunately, 1,3-(ethoxy-2-hydroxy)-propane-2-ol and 1,3-(diethoxy-4-hydroxy)-propane-2-ol are not commercially available. They therefore have to be synthesised.

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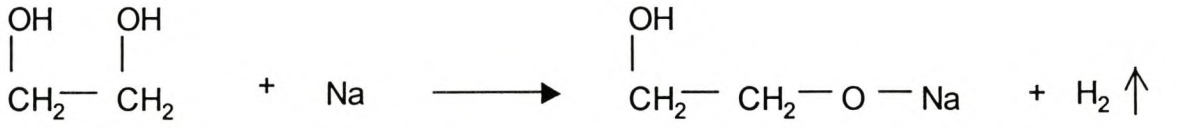
4.3 Synthesis of Optimum Solvents

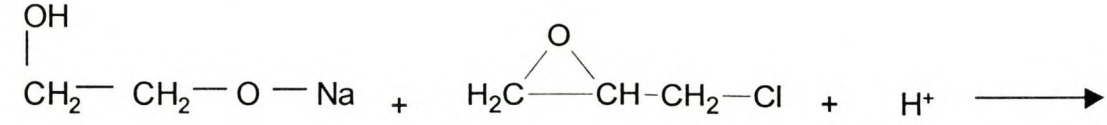
4.3.1 1,3-(ethoxy-2-hydroxy)-propane-2-ol

4.3.1.1 Reaction using Epichlorohydrin

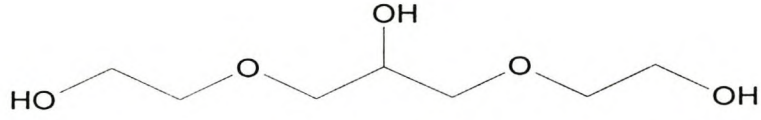
1,3-(ethoxy-2-hydroxy)-propane-2-ol was synthesised from ethylene glycol, sodium and epichlorohydrin according to the following two-step reaction:



Ethylene glycol Sodium metal Sodium 2-hydroxy-ethoxide Hydrogen gas (1)

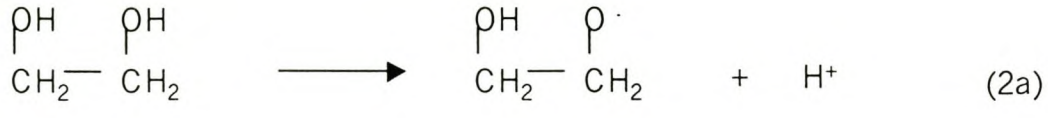


Sodium 2-hydroxy-ethoxide Epichlorohydrin Proton



1,3-(ethoxy-2-hydroxy)-propane-2-ol Sodium chloride (2)

The completion of step (2) relies on the donation of a proton from the reaction medium. In the case of ethylene glycol as reaction medium:



(2a)

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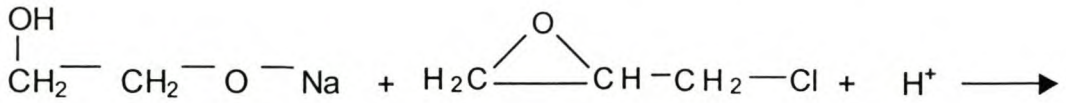
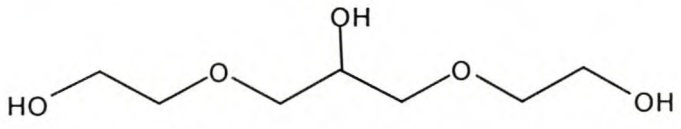


Sodium 2-hydroxy-ethoxide Epichlorohydrin proton



(2b)

1,3-di(ethoxy-2-hydroxy)-propane-2-ol sodium chloride sodium cation

(2c)

2-hydroxy-ethoxide ion sodium cation Sodium 2-hydroxy-ethoxide

4.3.1.2 Experimental Procedure

A four-necked two-litre flat-bottomed flask was positioned in a shallow water bath resting on a magnetic stirrer / heater. The first neck was fitted with a reflux water-condenser and the second with a thermometer. A gas inlet for the introduction of nitrogen was fitted to the third neck. A separating funnel was in turn fitted to the gas inlet and the fourth neck was closed with a stopper.

The experimental procedure was as follows:

1. 500 mL of anhydrous ethylene glycol was added to the dry flask. The ethylene glycol was dried prior to the synthesis by means of azeotropic distillation with benzene. The water content was measured by means of Karl Fischer titration as 0.048% by weight. The ethylene glycol added to the flask was far in excess of the stoichiometric amount required as it served both as the reaction medium and as a reagent.
2. A constant nitrogen gas flow into the reaction flask was maintained in order to prevent any air from coming into contact with the reaction mixture.
3. The sodium metal was cut into pieces of approximately 2 mm in diameter. During this procedure, the sodium metal was submerged in hexane so as to prevent oxidation of the clean metal surface.

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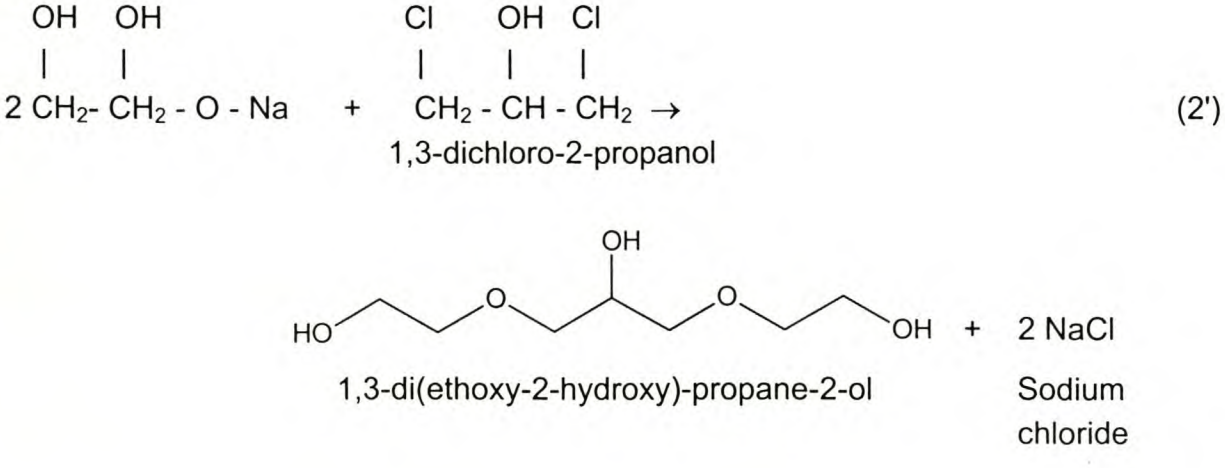
4. The sodium pieces were introduced into the stirred reaction mixture through the stoppered neck of the reaction flask. The reaction of sodium metal with the ethylene glycol is exothermic. The temperature of the reaction mixture was regulated by the water in the water bath, which was kept at a temperature of ~25°C.
5. The intermediate sodium salt formed in the first step of the reaction is unstable. Therefore, epichlorohydrin was slowly dripped into the reaction mixture through the separating funnel, immediately after the addition of sodium. An excess of 20% of epichlorohydrin was added.
6. After addition of the epichlorohydrin the reaction mixture was stirred for approximately fifteen hours to ensure that the reaction proceeded to completion.

Qualitative GC-MS results indicated that in addition to the desired product, a second high-boiling component was formed as a by-product. As the intermediate sodium compound is very unstable and as the second step of the reaction is considerably slower than the first step, the undesired by-product is almost certainly formed during the second step. Also, as the ethylene glycol reaction medium must donate a proton for the completion of the reaction, it is possible that the intermediate ion can react with the epichlorohydrin.

4.3.1.3 Reaction with 1,3-dichloro-2-propanol

The use of epichlorohydrin is undesirable not only because it requires proton donation from the ethylene glycol reaction mixture, but also because it is flammable, volatile, toxic and carcinogenic. It must consequently be handled with extreme care.

Therefore, epichlorohydrin was replaced with 1,3-dichloro-2-propanol in the second step of the reaction:



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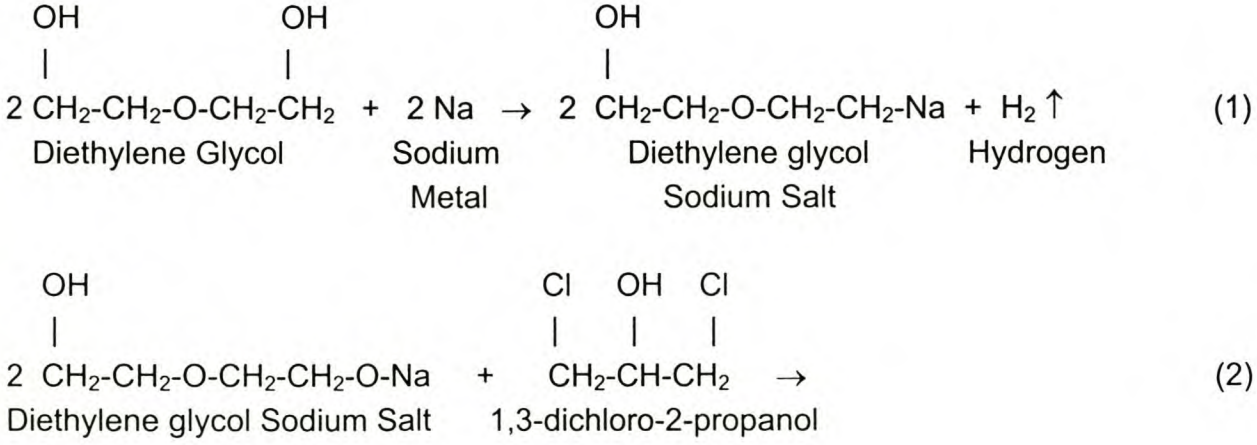
In this synthesis, the reaction medium is not required to donate a proton to complete the reaction.
In order to prevent formation of the by-product, the reaction mixture was heated to 40°C during the second step of the reaction and the rate of addition of 1,3-dichloro-2-propanol was substantially increased.

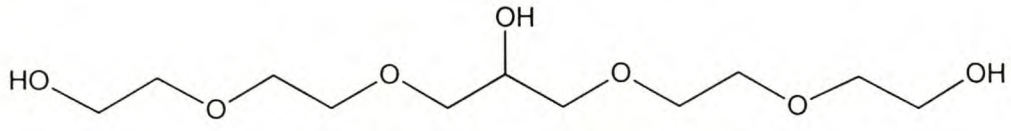
The amount of 1,3-dichloro-2-propanol added was reduced to approximately 60% of the required stoichiometric amount in order to minimise the possibility of side reactions occurring between excess reagent and any unknown intermediate ions in the reaction mixture. As a result a portion of the intermediate sodium product formed in the first step of the reaction remained unreacted. A dilute hydrochloric acid solution was therefore added to the final product to convert the sodium product back to ethylene glycol. Sodium chloride was formed as a by-product of this reaction.

By implementing these changes, the formation of the by-product was completely eliminated. The stoichiometric masses relevant to the synthesis are given in Appendix B1.

4.3.2 1,3-(Diethoxy-4-hydroxy)-propane-2-ol

The synthesis of 1,3-(diethoxy-4-hydroxy)-propane-2-ol is analogous to that of 1,3-(ethoxy-2-hydroxy)-propane-2-ol. The sole difference is that diethylene glycol replaces ethylene glycol as a reagent:





1,3-(Diethoxy-4-hydroxy)-propane-2-ol + 2 NaCl Sodium Chloride

The experimental apparatus and synthesis procedure are the same as those described for 1,3-(ethoxy-2-hydroxy)-propane-2-ol. The stoichiometric masses relevant to the synthesis are given in Appendix B2.

4.3.3 Purification of the Products

The resulting product mixture after synthesis consisted mainly of unreacted ethylene glycol and a significant amount of sodium chloride precipitate. The concentration of the desired solvent in the product mixture was estimated as approximately 10%.

A considerable amount of sodium chloride remained in solution. The first step in product purification was therefore the removal of the sodium chloride precipitate by means of filtration. After filtration, the water and hydrochloric acid were removed from the product mixture by means of vacuum distillation. The hydrochloric acid was removed along with the water in the distillate as a homogenous azeotrope. The last water was removed at an absolute pressure of 32 mbar and temperature of 110°C.

The product mixture was distilled further to remove the residual ethylene glycol as distillate. With the removal of the ethylene glycol, the solution of sodium chloride in the residue became supersaturated. This led to precipitation of the sodium chloride, which severely hampered the distillation process. Therefore, at a temperature of 135°C and pressure of 14 mbar, the distillation process was halted and the residue was filtered.

The viscosity of both synthesised solvents, as well as that of ethylene glycol and diethylene glycol, is extremely high. A significant residue of the product mixture therefore adhered to the sodium chloride in the filter cake. The synthesised solvents as well as ethylene glycol and diethylene glycol are readily soluble in 2-propanol and n-buthanol. Sodium chloride is not. The filter cake was therefore washed with a mixture of 2-propanol and n-butanol in order to recover any residual product adhering to the filter cake. The alcohol mixture was evaporated from the filtrate under vacuum in a standard Rotavap apparatus.

Mono- and diethylene glycol both form a heterogenous azeotrope with tridecane. Tridecane was therefore added to the product mixture which was distilled in a round-bottomed flask connected to a Dean-Stark water estimator and Liebig cooler. The ethylene glycol and diethylene glycol were removed as distillate along with the tridecane. The distillate formed two immiscible liquid phases in the arm of the Dean-Stark water estimator and could thus be recovered separately.

The residuaL tridecane in the product mixture was in turn removed by means of heterogenous azeotropic distillation with water, using the same apparatus. The water and tridecane in the distillate also formed two immiscible liquid phases and were recovered separately.

The final product was analysed qualitatively on an HP 5890A GC-MS and quantitatively on an HP 5890A GC with an FID detector. Quantitative GC analyses showed a single peak at a retention time that coincided with that of the synthesised solvent as identified on the GC-MS. Standard solutions of the components that were used in the synthesis and purification of the synthesised solvents were analysed in order to ascertain the retention times of these components and ensure that they did not coincide with that of the synthesised solvent peak. The temperature program was varied in order to vary the retention time of the synthesised solvent peak and in this way ensure that it did not coincide with any unknown impurity peaks.

The water content of the product was determined by means of Karl Fischer volumetric titrations using a Metrohm 701 Titrino.

After purification the 1,3-(ethoxy-2-hydroxy)-propane-2-ol product consisted of 89.7% 1,3-(ethoxy-2-hydroxy)-propane-2-ol and 10.3% water.

The final purified 1,3-(diethoxy-4-hydroxy)-propane-2-ol product consisted of 87.9% 1,3-(diethoxy-4-hydroxy)-propane-2-ol and 12.1% water. As water is added to the solvent system as a co-solvent, removal of the residual water was unnecessary.

4.4 Experimental verification of synthesised solvent's performance

The performance of the two synthesised solvents were investigated by means of batch extractions. Two different feed streams were used in these extractions, namely:

1. m-Cresol and o-tolunitrile in a mass ratio of 5:1
2. 2,4-Xylenol, o-tolunitrile and o-toluidine in a mass ratio of 4:1:1

The solvents were evaluated according to the recovery of larger phenolic molecules such as m-cresol and 2,4-xylenol, rather than phenol, because the recovery of the larger molecules is expected to be more sensitive to solvent molecule size.

The solvents are also evaluated on the basis of the number of moles of phenolic compound recovered in the solvent phase per number of moles of solvent used in the batch extraction.

The selectivity of the solvents for phenolic compounds over aromatic amines and nitriles was evaluated on the basis of m-cresol-o-tolunitrile, 2,4-xylenol-o-tolunitrile and 2,4-xylenol-o-toluidine separation factors.

Results are summarised in Table 4-2 and Table 4-4. Equilibrium compositions are given in Appendix A2.

As 1,3-(ethoxy-2-hydroxy)-propane-2-ol was synthesised from ethylene glycol and 1,3-(diethoxy-4-hydroxy)-propane-2-ol from diethylene glycol, they will be referred to as the *ethylene glycol-derivative* and the *diethylene glycol derivative* respectively in further discussion.

Table 4-2. Comparison of synthesised and commercial solvent performance at constant solvent mass ratios.

Exp. ID.	Solvent	$\beta_{m\text{-Cresol}}$ o-tolunitrile	$\beta_{2,4\text{-Xylenol}}$ o-tolunitrile	$\beta_{2,4\text{-Xylenol}}$ o-toluidine	$R_{o\text{-tolunitrile}}$ [%]	$R_{o\text{-toluidine}}$ [%]	$R_{phenolic}$ [%]	$n^{I}_{Phenolic} / n^{I}_{Solvent}$
Feed Stream 1: Solvent : Feed = 1.0; Hexane : Feed = 4.0; Water : Solvent = 0.11 (Mass Ratios)								
s1a	EGd*	8.9	n/a	n/a	45.7	n/a	88.2	1.2
s1b	TEG	17.8	n/a	n/a	53.3	n/a	95.3	1.0
s1g	DiEGd**	15.3	n/a	n/a	47.9	n/a	93.4	1.9
s1c	Tetra EG	17.0	n/a	n/a	48.9	n/a	94.2	1.4
s1e	Tetraglyme	4.2	n/a	n/a	59.4	n/a	86.1	1.5
s1d	Glycerol	8.5	n/a	n/a	31.8	n/a	79.9	0.6
s1f	Methanol	2.3	n/a	n/a	62.1	n/a	79.1	0.2
Feed Stream 2: Solvent : Feed = 3.0; Hexane : Feed = 4.0; Water : Solvent = 0.3 (Mass Ratios)								
s2b	TEG	n/a	14.1	3.7	47.4	77.5	92.7	0.3
s2a	DiEGd	n/a	12.9	3.4	41.3	72.6	90.0	0.4
s2c	Tetra EG	n/a	16.2	4.0	49.3	80.0	94.0	0.3
s2d	Glycerol	n/a	8.7	1.1	1.0	7.2	8.0	0.0
Feed Stream 2: Solvent : Feed = 2.0; Hexane : Feed = 4.0; Water : Solvent = 0.11 (Mass Ratios)								
s3b	TEG	n/a	12.6	3.5	53.9	80.6	93.6	0.4
s3a	DiEGd	n/a	12.3	3.7	47.3	74.8	91.7	0.7
s3c	Tetra EG	n/a	32.3	9.7	52.8	78.9	97.3	0.7
s3e	Tetraglyme	n/a	2.5	1.4	65.4	76.7	82.3	0.6
s3d	Glycerol	n/a	5.0	1.2	0.9	3.6	4.5	0.0
s3f	Methanol	n/a	1.8	0.8	74.3	87.1	83.9	0.3

From Table 4-2 it is clear that the ethylene glycol derivative performs very poorly in comparison with triethylene glycol - both with regard to selectivity and phenolic recovery. The phenolic recovery achieved with the ethylene glycol derivative is

however considerably better than that achieved with glycerol. A comparison of the performance of glycerol, the ethylene glycol derivative and the diethylene glycol derivative confirms the hypothesis that an increase in the number of ether groups between adjacent hydroxyl groups increases solvent performance.

As it was clear from the first set of batch extractions that the ethylene glycol derivative was significantly less effective than triethylene glycol, further synthesis thereof for additional batch extractions was not justified.

The diethylene glycol derivative performs well in comparison to triethylene glycol at equivalent solvent mass ratios. As the molar mass of the diethylene glycol derivative (M_r = 268.1) is almost double that of triethylene glycol (M_r = 150.17), the number of moles of solvent in the batch extractions differs considerably. The evaluation of relative solvent performance on a molecular level, is therefore more meaningful when based on batch extractions with equal molar ratios.

The solvents being compared are all high-boiling solvents, i.e. they are less volatile than the phenolic compounds in the feed. As such, the phenolic compounds will be recovered as distillate and the solvent as bottoms product during solvent recovery. Higher solvent mass ratios are therefore justified if the improved molar recovery of the phenolic compounds can be achieved without sacrificing selectivity.

The three most effective solvents tested are clearly the diethylene glycol derivative, tri- and tetraethylene glycol. The final batch extraction using triethylene glycol shown in Table 4-3 (experiment s7b) formed three liquid phases. The data obtained for the corresponding diethylene glycol derivative and tetraethylene glycol extractions (experiments s7a and s7d respectively) are therefore not incorporated in the average values shown in Table 4-4 as there are no quantitative values available for triethylene glycol.

While it has already been shown that the efficiency of a solvent cannot be based purely on the numerical ratio of ether to hydroxyl functional groups in the solvent molecule, it is interesting to note that this ratio lies between 1.0 and 3.0 for the most effective solvents tested. In increasing order, the ratios for the effective solvents are: 1.0 for triethylene glycol, 1.67 for the diethylene glycol derivative, 2.0 for tetraethylene glycol and 3.0 for triethylene glycolmonomethylether. The corresponding ratios for the more inefficient solvents are: 0.67 for the ethylene glycol derivative, 0.0 for both methanol and glycerol and 5.0 for tetraglyme.

Table 4-3. Comparison of synthesised and commercial solvent performance at constant solvent molar ratios.

Exp. ID.	Solvent	$\beta_{m\text{-Cresol}}$ o-tolunitrile	$\beta_{2,4\text{-Xylenol}}$ o-tolunitrile	$\beta_{2,4\text{-Xylenol}}$ o-toluidine	$R_{o\text{-tolunitrile}}$ [%]	$R_{o\text{-toluidine}}$ [%]	$R_{phenolic}$ [%]	$n^{I}_{Phenolic} / n^{I}_{Solvent}$
Feed Stream 1: Solvent : Feed = 0.6; Hexane : Feed = 5.0; Water : Solvent = 1.4 (Molar Ratios)								
s1a	Egd	8.9	n/a	n/a	45.7	n/a	88.2	1.2
s4a	TEG	13.1	n/a	n/a	54.3	n/a	93.9	1.3
s4e	DiEGd	19.1	n/a	n/a	50.2	n/a	95.1	1.3
s4b	Tetra EG	16.5	n/a	n/a	55.4	n/a	95.3	1.3
s4d	Tetraglyme	3.3	n/a	n/a	60.0	n/a	83.2	1.1
s4c	Glycerol	3.8	n/a	n/a	28.5	n/a	60.1	0.8
s4f	Methanol	2.2	n/a	n/a	47.7	n/a	67.0	0.8
Feed Stream 2: Solvent : Feed = 1.35; Hexane : Feed = 5.6; Water : Solvent = 5.0 (Molar Ratios)								
s5a	TEG	n/a	9.1	2.8	45.0	63.5	83.1	0.4
s2a	DiEGd	n/a	12.9	3.4	41.3	72.6	90.0	0.4
s5b	Tetra EG	n/a	11.8	3.5	44.8	73.4	90.5	0.4
s5d	Tetraglyme	Three Liquid Phases Formed						
s5c	glyc	n/a	12.1	1.1	0.2	2.1	2.3	0.0
s5e	MeOH	n/a	5.1	0.7	0.4	3.1	2.1	0.0
Feed Stream 2: Solvent : Feed = 0.95; Hexane : Feed = 5.4; Water : Solvent = 2.0 (Molar Ratios)								
s6d	triEG	n/a	10.2	4.2	47.9	69.1	90.3	0.6
s3a	DiEGd	n/a	12.1	3.7	47.5	74.7	91.6	0.7
s6c	tetraEG	n/a	10.4	3.7	48.7	72.8	90.8	0.6
s6b	Tglyme	Three Liquid Phases Formed						
s6a	Glycerol	n/a	8.0	1.0	0.2	1.9	1.9	0.0
s6e	Methanol	n/a	4.2	0.8	0.2	1.3	1.0	0.0
Feed Stream 1: Solvent : Feed = 0.8; Hexane : Feed = 3.0; Water : Solvent = 7.5 (Molar Ratios)								
s7b	TEG	Three Liquid Phases Formed						
s7a	DiEGd	n/a	7.7	2.9	51.4	73.9	89.0	0.7
s7d	Tetra EG	n/a	7.4	2.7	51.8	74.7	88.9	0.7
s7e	Tetraglyme	Three Liquid Phases Formed						
s7f	Methanol	n/a	4.2	0.6	0.5	3.1	2.0	0.0

*EGd = 1,3-(ethoxy-2-hydroxy)-propane-2-ol; **DiEGd = 1,3-(diethoxy-4-hydroxy)-propane-2-ol

Table 4-4: Summary of solvent performance based on constant molar ratio.

Solvent	$\beta_{m\text{-Cresol}}$ o-tolunitrile	$\beta_{2,4\text{-Xylenol}}$ o-tolunitrile	$\beta_{2,4\text{-Xylenol}}$ o-toluidine	$R_{o\text{-tolunitrile}}$ [%]	$R_{o\text{-toluidine}}$ [%]	$R_{m\text{-Cresol}}$ [%]	$R_{2,4\text{-Xylenol}}$ [%]	$n^{l}_{m\text{-Cresol}} / n^{l}_{Solvent}$	$n^{l}_{2,4\text{-Xylenol}} / n^{l}_{Solvent}$
EGd	8.9	n/a	n/a	45.7	n/a	88.2	n/a	1.2	n/a
TEG	13.1	9.6	3.5	49.0	66.3	93.9	86.7	1.2	0.4
DiEGd	19.1	12.5	3.5	46.3	73.7	95.1	90.8	1.6	0.6
Tetra EG	16.5	11.1	3.6	49.6	73.1	95.3	90.7	1.3	0.5
Tetraglyme	3.3	n/a	n/a	60.0	n/a	83.2	n/a	1.3	n/a
Glycerol	3.8	10.1	1.1	9.6	2.0	60.1	2.1	0.7	0.02
Methanol	2.2	4.7	0.7	16.1	2.2	67.0	1.6	0.5	0.1

From Tables 4-2, 4-3 and 4-4 it can be seen that the number of moles of m-cresol and 2,4-xylenol recovered per mole of solvent is highest for the diethylene glycol derivative for all the solvent ratios tested. The recovery of m-cresol and 2,4-xylenol achieved with the diethylene glycol derivative is consequently noticeably higher than that achieved with triethylene glycol.

The recovery of o-tolunitrile is lower in the batch extractions using the diethylene glycol derivative than in those using tri- or tetraethylene glycol. The best separation achieved between the phenolic compounds and o-tolunitrile is consequently that achieved with the diethylene glycol derivative.

Unfortunately, the recovery of o-toluidine is noticeably higher in the diethylene glycol derivative extractions than in the triethylene glycol extractions. At high water to solvent molar ratios (5.0 and 7.5) the o-toluidine recovery achieved with the diethylene glycol derivative is lower than that achieved with tetraethylene glycol. At a low water to solvent molar ratios (2.0), the opposite is true.

The 2,4-xylenol - o-toluidine separation factors achieved with the diethylene glycol derivative and triethylene glycol are on average equal, while higher phenolic recovery, m-cresol - o-tolunitrile and 2,4-xylenol - o-tolunitrile separation factors are obtained with the diethylene glycol derivative. The diethylene glycol derivative also appears to be less prone to three phase formation.

It can therefore be concluded that the diethylene glycol derivative outperforms triethylene glycol in most respects, on a molar basis over the limited range of solvent ratios tested. However, the difference in solvent performance is small and triethylene glycol is relatively inexpensive and readily available. Triethylene glycol was therefore chosen as the solvent to be used in the further optimisation of the proposed solvent system.

CHAPTER 5. INVESTIGATION OF SOLVENT SYSTEM WITH SINGLE-STAGE EXTRACTIONS

5.1 Introduction

In Chapters 3 and 4 it was determined that a solvent system consisting of triethylene glycol, water and hexane is effective in the separation of phenolic compounds from neutral oils and nitrogen bases. During the solvent selection process, batch extractions were performed at selected solvent ratios on one of the three synthetic feed streams listed in Table 3-1. A more thorough investigation of the solvent system is required for further development of the proposed separation process.

To this end, batch extractions were performed on each of the three synthetic feed streams listed in Table 3-1. The aim of these extractions was twofold: to determine the effect of the various solvent ratios on phenolic recovery and separation efficiency, and to generate liquid-liquid equilibrium data for thermodynamic modelling.

The optimum solvent to feed, hexane to feed and water to solvent ratios for a single stage extraction can be identified by determining the effect of these solvent ratios on phenolic recovery and the separation efficiency.

It is important to note that both recovery and separation efficiency should be investigated. A system that yields a good separation efficiency may yield such a low recovery that extreme phase ratios may be necessary to obtain a satisfactory recovery. This may be impractical due to either technical or economic reasons.

After the optimum single-stage solvent ratios have been determined, they can then be used as a starting point for the optimisation of a multistage extraction process.

The multistage extraction process can be optimised further by means of pilot plant tests and simulations. A thermodynamic model is required as a basis for the simulations. Such a thermodynamic model can be obtained by regression of the batch extraction data. It was therefore imperative that enough LLE data be generated with the batch extractions to fit a model. Furthermore, the LLE data had to encompass a wide range of solvent ratios so that the fitted model could be used for interpolation only.

The interaction between the various feed components and the solvent system could also be illustrated using the batch extraction data.

5.2 Batch Extractions

A series of batch extraction tests were carried out on each of the three synthetic feed streams listed in Table 3-1. The synthetic feed streams were investigated separately in order to facilitate analysis and a better understanding of the interaction of each type of feed component with the solvent system. The compositions of the feed streams were kept constant as specified in Table 3-1 for each series of batch extractions.

The solvent to feed, water to solvent and hexane to feed ratios were varied over the ranges 0.5 to 3.0, 0.5 to 5.0 and 0.0 to 1.0 respectively. Higher solvent ratios than those listed were considered impractical in terms of the cost of solvent recovery in a commercial process and were therefore not investigated.

The apparatus and procedure used in these series of batch extractions was identical to that used in the batch extractions for solvent screening (Section 3.5.1).

5.3 Analysis

The liquid phases resulting form the batch extractions were analysed on a Hewlett-Packard 5890A gas chromatograph (GC) with a flame-ionisation detector (FID). A 60 m Zebron D68H5 capillary column (inner diameter 0.25 mm) was used. Response factors were determined using solutions of known concentrations which included internal standards. The selection of the internal standards is critical to the accuracy of the analysis results, and will therefore be discussed in more detail.

The interaction between the various components in the synthetic feed streams and the stationary phase of the GC capillary column is such that the shape of the component peaks and retention times vary considerably. In addition, while the FID detects no water peak, the concentration of water in the analysis sample has a noticeable effect on the response factors of the phenolic compounds, nitrogen bases and TEG. The response factors of the neutral oils remain unaffected by the water concentration.

Therefore, a known amount of water was added to the standard solutions used for calibration and two different internal standards were used for each sample. The response factor of the first, toluene, is unaffected by water and was used for the calculation of the concentrations of hexane and neutral oils such as mesitylene, pseudocumene, undecane and dodecane. The retention times and peak shapes of these components and toluene are similar.

The second internal standard was a phenolic compound, either m-cresol or 2,4-xylenol, and was used for the calculation of the phenolic and nitrogen compound concentrations. The peak shapes and retention times of the phenolic compounds and nitrogen bases are similar. The phenolic compound selected as an internal standard for a specific sample depended on the feed stream used in the generation of the sample. Thus, m-cresol was the standard used for samples generated using the phenol and xylenol feed streams and 2,4-xylenol was used as a standard for those generated with the m-cresol feed stream. By this method it was ensured that the effect of water on the response factor of a given component was the same as on the response factor of the internal standard used to calculate the concentration of the given component.

The peak width, volatility and retention time of the various components were also similar to those of the internal standard used to calculate their concentration. Thus, discrepancies in analysis due to effects such as discrimination between components in the injector were largely eliminated.

The water content of both the solvent and hexane phases was determined by means of volumetric Karl Fischer titrations using a Metrohm 701 Titrino.

Each of the GC and Karl Fischer analyses was repeated at least twice to ensure repeatability.

The accuracy of the analysis results was evaluated on the basis of mass balances over each component in the resulting phases. The percentage error in the mass balance for a component i is defined as:

$$\varepsilon_i = \frac{m_i^{IN} - m_i^{I} - m_i^{II}}{m_i^{IN}} x100 \qquad [\%] \qquad (5.3\text{-}1)$$

where

ε_i	:	percentage error
$m^{IN}{}_i$	:	measured mass of component i added to batch extraction
m^{I}_i	:	analytically determined mass of component i in the extract phase
m^{II}_i	:	analytically determined mass of component i in the hexane phase

The average absolute percentage errors in the mass balances over the components used in the batch extraction tests are listed in Table 5-1. The discrepancies in the mass

balances over each component for each individual batch extraction are listed in Appendix A.

Table 5-1. Average percentage errors, ε_i, in the mass balances over the individual components present in the resulting phases of the batch extraction tests.

Phenol Feed Stream		m-Cresol Feed Stream		Xylenol Feed Stream	
Component i	ε_i [%]	Component i	ε_i [%]	Component i	ε_i [%]
Mesitylene	1.3	Pseudocumene	0.8	Indane	1.2
5-Et-2-me-pyridine	1.5	Undecane	1.0	Dodecane	1.2
Benzonitrile	1.4	Indene	0.8	Naphthalene	1.2
Aniline	1.3	o-Tolunitrile	0.8	2,4-Xylenol	1.4
Phenol	1.7	o-Toluidine	0.7	3,4-Xylenol	1.3
		m-Cresol	1.0	3,5-Xylenol	1.3
Solvents					
Triethylene glycol	1.3	Water	1.2	Hexane	1.6

The measured mass of the extract phase differed from the sum of the analytically determined masses of the constituent components by ±1.2 % on average. The corresponding difference for the hexane phase was ±1.7 % on average. Overall mass balances for each batch extraction yielded an average error of 1.7%.

5.4 Results

The ultimate aim of this study is to develop a process that can be commercially implemented for the separation of phenolic compounds from neutral oils and nitrogen bases. A high phenolic recovery and purity is essential for the commercial success of such a process. I.e. a high phenolic recovery and, simultaneously, a high degree of separation between the individual phenolic compounds and neutral oils / nitrogen bases must be achieved. Another factor of commercial importance is the solvent ratios required to achieve a satisfactory phenolic recovery and separation efficiency as very high solvent ratios result in high solvent recovery costs.

The degree of separation obtained between the phenolic compounds and neutral oils / nitrogen bases can be illustrated in terms of the appropriate separation factors. The phenolic recovery can be illustrated in terms of the percentage recovery of each phenolic compound in the extract phase. The batch extraction results are therefore

presented in the form of separation factors and percentage recovery of phenolic compounds in the extract phase as a function of solvent to feed, hexane to feed and water to solvent ratios.

The individual phenolic recoveries and separation factors are presented separately in order to facilitate an understanding of the interaction between each type of component and the solvent system.

In all Tables and Figures, the abbreviations S/F, H/F and W/S are used in place of triethylene glycol to feed, hexane to feed and water to solvent mass ratios respectively. The term, solvent, is used for triethylene glycol alone and does not refer to a mixture of triethylene glycol and water. The term, feed, is used for the mixture of phenolic compounds, neutral oils and nitrogen bases that is contacted with triethylene glycol, water and hexane in each series of batch extractions.

The term solvent phase refers to the liquid phase containing the bulk of the triethylene glycol and water in the system. As the phenolic compounds are recovered in this phase, it is also referred to as the extract phase. The hexane phase refers to the phase containing the bulk of the hexane in the system.

The terms, component recovery and percentage of feed component remaining in the solvent phase, are synonymous. The latter is more often used to refer to the recovery of neutral oils and nitrogen bases.

The masses of all the components added to each batch extraction as well as the masses of the components in the corresponding resulting phases for the batch extraction using the phenol, m-cresol and xylenol feed streams are listed in Appendices A3, A4 and A5 respectively.

The effect of solvent ratios on phenolic recovery, separation factors and percentage of neutral oils and nitrogen bases remaining in the solvent phase are discussed in more detail in the subsequent sections.

5.4.1 Phenolic Recovery

5.4.1.1 Phenol Recovery

Phenol recoveries, phenol-mesitylene, phenol-benzonitrile, phenol-aniline and phenol-5-et-2-me-pyridine separation factors, as well as the percentage of feed mesitylene, benzonitrile, aniline and 5-et-2-me-pyridine remaining in the extract phase are listed for various solvent to feed, water to solvent and hexane to feed mass ratios in Table 5-2.

Table 5-2 shows that excellent recoveries are obtained for phenol at most solvent ratios. Phenol recoveries smaller than 90% are obtained only at very low solvent to feed ratios of 0.5 combined with high water to solvent or hexane to feed ratios. Recoveries as high as 99.1% are achieved.

The effect of the solvent to feed ratio on the phenol recovery is illustrated in Figure 5.4-1. It is clear that an increase in the solvent to feed ratio without exception leads to an increase in phenol recovery at a constant water to solvent and hexane to feed ratios. At low hexane to feed ratios of 0.5 and 1.0, this increase is slight. However, as the hexane to feed ratio is increased first to 3.0 and then 5.0, the increase in phenol recovery with an increase in solvent to feed ratio is more significant.

Table 5-2. Percentage recovery of phenol, R_{Phenol}; phenol-mesitylene, phenol-aniline, phenol-benzonitrile and phenol-5-et-2-me-pyridine separation factors, $\beta_{Phenol\text{-}Mesitylene}$, $\beta_{Phenol\text{-}Aniline}$, $\beta_{Phenol\text{-}Benzonitrile}$, $\beta_{Phenol\text{-}Et\text{-}me\text{-}pyridine}$; and percentage of feed neutral oils and nitrogen bases remaining in the extract phase, $R_{Mesitylene}$, $R_{Aniline}$, $R_{Benzonitrile}$, $R_{Etmepyridine}$; for the system Hexane + Water + Mesitylene + Aniline + Benzonitrile + 5-Et-2-me-pyridine + Phenol + Triethylene Glycol at various Solvent to Feed, S/F, Hexane to Feed, H/F, and Water to Solvent, W/S, mass ratios. Temperature 40 °C and Pressure101.3 kPa.

Exp.	Mass Ratios			R_{Phenol}	$\beta_{Phenol\text{-}Mesitylene}$	$\beta_{Phenol\text{-}Aniline}$	$\beta_{Phenol\text{-}Benzonitrile}$	$\beta_{Phenol\text{-}Etmepyridine}$	$R_{Mesitylene}$	$R_{Aniline}$	$R_{Benzonitrile}$	$R_{Etmepyridine}$
ID	S/F	H/F	W/S	[%]					[%]	[%]	[%]	[%]
1A	1.0	3.0	0.3	93.9	341.0	2.6	9.2	17.5	4.4	85.6	62.8	47.0
1B	1.0	1.0	0.3	96.9	209.0	2.2	7.1	13.0	13.1	93.6	81.6	70.8
1C	1.0	0.5	0.3	98.0	149.9	2.0	6.1	11.9	24.6	96.1	88.9	80.5
1D	1.5	4.9	0.7	90.6	726.8	2.9	12.9	25.4	1.3	77.0	42.9	27.6
2A	1.0	4.9	0.3	92.4	413.2	2.9	10.1	23.2	2.9	80.8	54.7	34.4
2B	1.0	1.0	0.7	95.9	264.4	1.9	7.2	13.3	8.2	92.6	76.6	63.9
2C	1.0	0.5	0.7	96.8	169.1	2.2	6.2	12.6	15.1	93.3	83.0	70.5
2D	1.0	3.0	0.7	92.3	371.4	2.5	9.3	18.7	3.1	82.7	56.3	39.0
3A	0.5	0.5	0.7	96.6	85.8	2.2	4.4	9.6	24.7	92.9	86.4	74.6
3B	1.5	0.5	0.7	97.0	235.8	2.2	7.5	14.0	12.0	93.5	81.2	69.6
3C	2.0	0.5	0.7	97.3	333.0	1.7	8.5	17.3	9.7	95.5	80.7	67.4
3D	3.0	0.5	0.7	98.0	477.6	1.6	9.3	18.9	9.4	97.0	84.3	72.4
4A	0.5	3.0	0.7	89.8	211.4	1.9	6.2	13.6	4.0	82.3	58.5	39.3
4B	1.5	3.0	0.7	93.0	587.1	2.4	9.8	24.0	2.2	84.7	57.6	35.6
4C	2.0	3.0	0.7	93.5	679.0	2.3	10.2	27.1	2.1	86.1	58.5	34.6
4D	3.0	3.0	0.7	95.3	723.4	2.6	13.3	33.1	2.7	88.6	60.2	37.8
5A	1.0	1.0	0.1	97.2	139.6	2.1	6.7	11.3	19.9	94.2	83.8	75.3
5B	1.0	0.5	0.1	98.3	117.2	1.8	5.7	9.4	33.1	96.9	91.0	86.0
5C	1.5	3.0	0.1	95.4	240.3	2.6	9.3	18.1	8.0	88.9	69.1	53.5
5D	1.0	5.0	0.1	91.5	258.2	2.9	8.7	16.7	4.0	78.9	55.4	39.3
6A	0.5	3.1	0.1	90.4	123.8	2.0	5.5	9.2	7.1	82.2	63.1	50.8
6B	1.0	3.0	0.1	94.6	202.6	2.6	8.2	14.5	7.9	87.1	68.0	54.5
6C	2.0	3.0	0.1	95.9	217.0	3.0	10.9	19.5	9.8	88.6	68.3	54.8
6D	3.0	3.0	0.1	97.8	331.0	3.3	14.2	26.3	11.8	93.1	75.7	62.7
7A	0.5	4.9	0.7	86.1	238.0	2.5	7.1	13.5	2.5	71.1	46.6	31.6
7B	1.0	4.9	0.7	90.1	485.8	2.9	11.4	24.1	1.8	75.9	44.4	27.4
7C	2.0	5.0	0.7	91.6	735.3	3.0	13.6	27.5	1.5	78.3	44.6	28.4
7D	3.0	5.0	0.7	93.9	624.5	3.1	16.2	33.8	2.4	83.2	48.8	31.4
8A	0.5	1.0	0.7	94.5	118.2	1.6	4.8	8.1	12.8	91.4	78.3	68.2
8B	1.5	1.0	0.7	95.9	314.6	1.9	7.7	16.1	6.9	92.5	75.1	59.0
8C	2.0	1.1	0.7	96.3	464.4	1.9	8.8	18.4	5.2	93.1	74.5	58.2
8D	3.0	0.8	0.7	97.5	502.5	1.8	9.6	19.3	7.2	95.6	80.4	67.0
8E	3.0	1.0	0.7	97.3	635.1	1.9	10.1	21.6	5.3	94.9	77.8	62.2
9A	0.5	3.0	0.3	90.5	162.9	1.9	5.6	9.6	5.5	83.5	63.0	49.9
9B	1.5	3.0	0.3	94.6	385.6	2.6	10.1	18.9	4.3	86.9	63.3	47.8
9C	2.0	3.1	0.3	95.6	672.0	2.9	11.3	22.8	3.1	88.3	65.8	48.9
9D	3.0	3.0	0.3	97.1	716.4	3.1	14.5	29.6	4.4	91.6	69.6	53.0

Table 5-2 (continued).

Exp.	Mass Ratios			R_{Phenol}	$\beta_{Phenol\text{-}Mesitylene}$	$\beta_{Phenol\text{-}Aniline}$	$\beta_{Phenol\text{-}Benzonitrile}$	$\beta_{Phenol\text{-}Etmepyridine}$	$R_{Mesitylene}$	$R_{Aniline}$	$R_{Benzonitrile}$	$R_{Etmepyridine}$
ID	s/f	h/f	w/s	[%]					[%]	[%]	[%]	[%]
10A	1.5	1.0	0.3	97.4	268.6	2.2	7.9	15.1	12.2	94.4	82.4	71.1
10B	0.5	1.0	0.3	95.5	96.7	1.9	4.6	7.6	18.0	92.0	82.3	73.8
10C	2.0	1.0	0.3	97.9	389.1	2.2	9.1	17.8	10.7	95.5	83.7	72.3
10D	2.9	1.0	0.3	98.5	480.7	2.2	11.1	21.5	11.7	96.6	85.1	74.8
11A	1.5	0.5	0.3	98.5	235.5	1.9	7.3	13.1	21.6	97.1	89.9	83.2
11B	0.5	0.5	0.3	97.4	81.4	1.6	4.0	6.4	31.8	95.9	90.5	85.6
11C	2.0	0.5	0.3	98.6	298.1	1.9	8.3	15.3	19.4	97.4	89.6	82.5
11D	3.0	0.5	0.3	99.1	436.3	2.0	9.1	17.5	19.6	98.2	92.1	85.9
12A	1.5	1.0	0.1	98.2	205.0	2.4	8.7	15.0	21.0	95.7	86.2	78.4
12B	2.0	1.0	0.1	98.6	253.3	2.4	8.8	17.6	21.3	96.6	88.6	79.5
12C	0.5	1.0	0.1	95.8	86.7	1.9	4.4	6.5	20.9	92.5	83.7	77.9
12D	3.0	1.0	0.1	98.9	311.5	2.4	10.9	21.2	23.1	97.5	89.5	81.5
13A	0.5	5.2	0.3	86.3	204.9	1.9	6.3	11.1	3.0	76.6	49.9	36.2
13B	1.5	5.0	0.3	93.5	616.3	3.3	13.0	23.7	2.3	81.6	52.6	37.8
13C	2.0	4.9	0.3	94.8	688.6	3.4	15.2	27.7	2.6	84.5	54.7	39.8
13D	3.0	5.0	0.3	96.1	842.6	3.6	17.1	32.7	2.8	87.2	58.9	42.9
14A	0.5	5.0	0.1	86.8	173.9	2.4	6.1	10.2	3.6	73.2	51.6	39.0
14B	1.5	4.9	0.1	94.5	342.7	3.3	11.8	22.4	4.8	84.1	59.4	43.6
14C	2.0	5.0	0.1	95.8	309.9	3.4	14.4	26.1	6.9	87.2	61.5	46.8
14D	3.0	5.0	0.1	97.2	329.6	3.7	17.0	30.3	9.4	90.2	66.9	53.1
15A	1.0	4.9	0.0	92.0	108.0	2.3	8.3	12.2	9.6	83.5	58.2	48.4
15B	1.5	5.0	0.0	94.8	123.5	2.8	10.4	18.3	12.9	86.8	63.8	50.1
15C	2.0	5.0	0.0	96.0	133.2	2.9	12.1	19.9	15.1	89.0	66.2	54.3
15D	3.1	5.0	0.0	96.8	131.6	2.6	11.2	21.0	18.8	92.2	73.2	59.2
16A	1.5	3.0	0.0	96.1	163.3	2.3	9.0	16.5	13.0	91.4	73.0	59.7
16B	2.0	3.0	0.0	97.2	203.3	2.9	11.4	20.9	14.7	92.3	75.4	62.6
16C	3.0	3.0	0.0	98.1	195.9	2.9	12.3	26.1	20.9	94.8	80.9	66.5
16D	1.0	3.0	0.0	93.9	125.9	2.3	7.0	10.3	10.8	87.1	68.7	59.8
17A	3.0	3.0	0.4	96.4	992.1	2.8	14.8	29.2	2.6	90.7	64.3	47.8
17B	3.1	3.0	0.6	96.9	1595.4	2.9	18.1	41.7	1.9	91.4	62.9	42.5
17C	2.0	3.0	0.4	95.7	796.5	2.8	13.8	28.4	2.7	89.1	62.1	44.2
17D	2.1	3.0	0.6	94.5	918.8	2.7	13.4	28.8	1.8	86.6	56.2	37.3
18A	1.0	3.0	0.3	91.6	261.9	2.3	7.9	13.8	4.0	82.9	57.9	44.2
18B	1.0	3.0	0.3	89.9	201.0	1.7	5.5	10.6	4.2	83.6	61.6	45.6
18C	1.0	3.0	0.4	92.5	296.0	1.9	7.4	14.0	4.0	86.4	62.2	46.7
18D	1.0	3.0	0.3	92.2	294.6	2.2	8.1	14.4	3.9	84.4	59.3	45.1
18E	1.0	3.0	0.3	93.4	332.9	2.4	9.6	15.5	4.1	85.3	59.7	47.8
19A	1.0	3.1	0.4	94.2	424.3	2.8	10.2	19.7	3.7	85.4	61.5	45.1
19B	1.0	3.0	0.6	92.9	428.2	2.9	9.4	21.0	3.0	82.0	58.3	38.5
19C	2.0	4.0	0.3	95.8	826.7	3.4	15.3	35.4	2.7	86.8	59.6	38.9
19D	1.4	4.1	0.3	94.3	569.4	3.1	13.3	28.0	2.8	84.1	55.3	37.0
19E	0.5	1.9	0.3	92.3	122.9	1.8	4.8	8.1	8.9	86.8	71.2	59.5

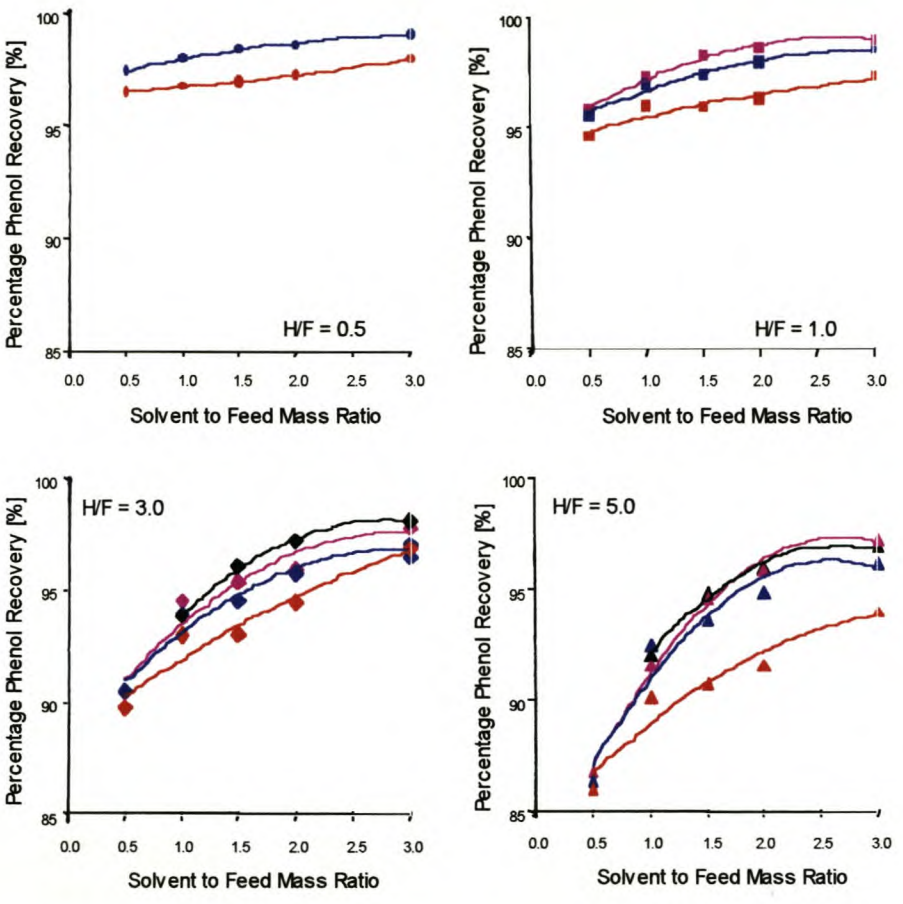


Figure 5.4-1. Effect of Solvent to Feed Ratio on Phenol Recovery at Selected Hexane to Feed and Water to Solvent ratios

● H/F=0.5; W/S=0.7 ● H/F=0.5; W/S=0.3
■ H/F=1.0; W/S=0.7 ■ H/F=1.0; W/S=0.3 ■ H/F=1.0; W/S=0.1
◆ H/F=3.0; W/S=0.7 ◆ H/F=3.0; W/S=0.3 ◆ H/F=3.0; W/S=0.1 ◆ H/F=3.0; W/S=0.0
▲ H/F=5.0; W/S=0.7 ▲ H/F=5.0; W/S=0.3 ▲ H/F=5.0; W/S=0.1 ▲ H/F=5.0; W/S=0.0

At higher hexane ratios of 3.0 and 5.0 the most significant increase in the phenol recovery occurs as the solvent to feed ratio is increased from 0.5 to 2.0. A further increase in the solvent to feed ratio leads to a more gradual increase in phenol recovery. With the exception of the extractions carried out at water to solvent ratios of 0.7, it appears that the maximum phenol recovery is achieved at a solvent to feed ratio of 3.0 and that a further increase beyond this point will not lead to any significant additional increase in phenol recovery.

At a constant hexane to feed and water to solvent ratios, the increase in phenol recovery with an increase in the solvent to feed ratio is to be expected. Phenol is soluble in both triethylene glycol and hexane. Two conflicting driving forces are

therefore exerted on the phenol molecule: one for the dissolution of phenol in triethylene glycol and the other for the dissolution of phenol in hexane. An increase in the solvent to feed ratio at constant hexane to feed ratio increases the ratio of triethylene glycol to hexane and thus increases the potential for a phenol molecule to dissolve in the triethylene glycol phase rather than the hexane phase.

An increase in the solvent to feed and therefore the triethylene glycol to phenol ratio also increases the number of triethylene glycol hydroxyl functional groups available for the formation of hydrogen bonds with the phenol molecule.

At low hexane to feed ratios, very little solvent is required to counteract the driving force for the dissolution of phenol in the hexane phase. Very little phenol is thus lost to the hexane phase. As phenol recovery is already very high, a further increase in the solvent to feed ratio can only increase the phenol recovery to a small extent.

On the other hand, at high hexane to feed ratios, the phenol recovery at low solvent to feed ratios will be considerably lower. A much larger proportion of phenol is thus present in the hexane phase. As the amount of phenol to be recovered from the hexane phase is larger, the increase in phenol recovery will thus be more significant than at low hexane to feed ratios.

As the amount of phenol in the hexane phase decreases with an increase in solvent to feed ratio, the ratio of hexane to phenol in the hexane phase obviously increases. This will continue until a point is reached where the ratio of hexane to dissolved phenol is so high that a proportionally larger increase in solvent to feed ratio is required to extract it from the hexane phase. The increase in phenol recovery with an increase in solvent to feed ratio can therefore be expected to become less significant as the phenol recovery becomes very high.

From Figure 5.4-1 it can also be seen that the phenol recoveries achieved in extractions at constant hexane and solvent to feed ratios are lower at higher water to solvent ratios. This effect will be discussed in more detail later.

The effect of the hexane to feed ratio on phenol recovery is illustrated in Figure 5.4-2.

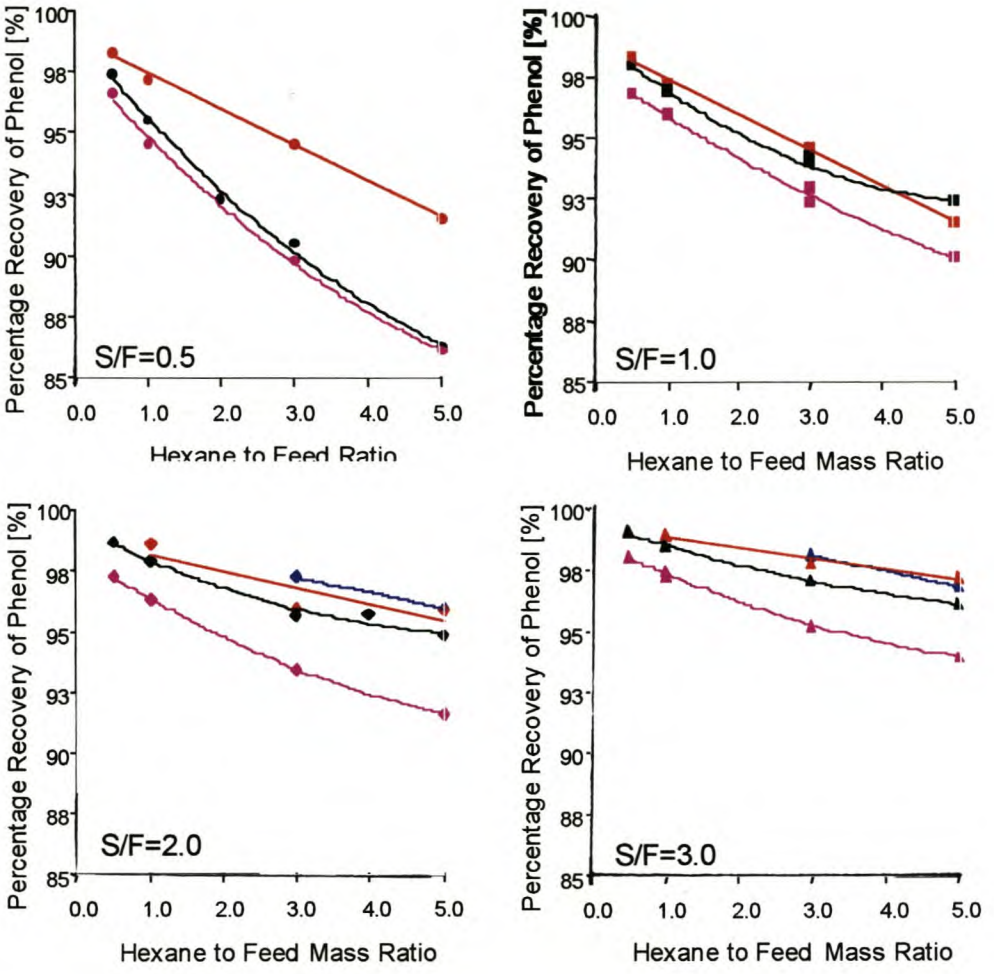


Figure 5.4-2. Effect of hexane to feed ratio on the phenol recovery at selected solvent to feed and water to solvent ratios.

● S/F=0.5; W/S=0.7 ● S/F=0.5; W/S=0.3 ● S/F=0.5; W/S=0.1
■ S/F=1.0; W/S=0.7 ■ S/F=1.0; W/S=0.3 ■ S/F=1.0; W/S=0.1
◆ S/F=2.0; W/S=0.7 ◆ S/F=2.0; W/S=0.3 ◆ S/F=2.0; W/S=0.1 ◆ S/F=2.0; W/S=0.0
▲ S/F=3.0; W/S=0.7 ▲ S/F=3.0; W/S=0.3 ▲ S/F=3.0; W/S=0.1 ▲ S/F=3.0; W/S=0.0

It is clear from Figure 5.4-2 that an increase in the hexane to feed ratio leads to a significant decrease in phenol recovery, especially at low solvent to feed ratios.

For example, at a solvent to feed ratio of 0.5 and a water to solvent ratio of 0.3, the phenol recovery decreases 11.1 percentage points from 97.4% to 86.3% as the hexane to feed ratio increases from 0.5 to 5.0. In contrast, at a solvent to feed ratio of 3.0 and a water to solvent ratio of 0.3, the phenol recovery decreases only 3.0 percentage points from 99.1% to 96.1% as the hexane to feed ratio is increased over the same range.

The decrease in phenol recovery with an increase in the hexane to feed ratio is to be expected for the same reason that an increase in the solvent to feed ratio can be expected to increase the phenol recovery.

The greater effect of the hexane to feed ratio on phenol recovery at low solvent ratios can best be explained with the help of Table 5-3.

Given that the percentage of phenol in the feed is 71% by mass, and given that there are two hydroxyl groups per triethylene glycol molecule, the number of solvent hydroxyl groups available for hydrogen bonding per phenol molecule may be calculated for various solvent to feed ratios. These values are illustrated in Table 5-3.

Table 5-3. Number of solvent hydroxyl groups per phenol molecule at various solvent to feed mass ratios.

Solvent to Feed Mass Ratio	TEG to Phenol Molar Ratio	Number of Solvent Hydroxyl Groups per Phenol Molecule
0.5	0.44	0.9
1.0	0.88	1.8
1.5	1.33	2.7
2.0	1.77	3.5
2.5	2.21	4.4
3.0	2.65	5.3

At a solvent to feed ratio of 0.5, there are marginally fewer solvent hydroxyl groups available for hydrogen bonding than there are phenol molecules. As such, some of the phenol molecules in the feed will not form hydrogen bonds with the triethylene glycol molecules in the solvent phase.

It must also be taken into consideration that, while two phenol molecules may ideally be accommodated by one triethylene glycol molecule, it is unlikely that this will occur as the hydroxyl groups of the phenol molecules must be correctly aligned to fully utilise each available triethylene glycol molecule. Thus the ratio of solvent hydroxyl groups to phenol molecules can be expected to be considerably larger than 1.0 to ensure that all phenol molecules will form hydrogen bonds.

Therefore, the proportion of phenol molecules that are not held in the solvent phase with hydrogen bonds will be higher at low solvent to feed ratios. These phenol molecules are therefore more susceptible to dissolution in the hexane phase than the hydrogen bound molecules. Therefore, an increase in hexane to feed ratio will have a greater effect on phenol recovery at low solvent to feed ratios

Table 5-4 shows the percentage point decrease in phenol recovery as the hexane to feed ratio is increased from 0.5 to 5.0 for a wider range of constant solvent to feed and water to solvent ratios. The corresponding decrease in phenol recovery as the hexane to feed ratio is increased from 3.0 to 5.0 is also illustrated.

As can be expected the hexane to feed ratio has the greatest impact on phenol recovery at low solvent ratios and this impact steadily decreases as the solvent ratio increases.

Both Figure 5.4-1 and Table 5-4 show that the effect of the hexane to feed ratio on phenol recovery is greater at higher water to solvent ratios.

Table 5-4. Percentage point decrease in phenol recovery as the hexane to feed ratio is increased from 0.5 to 5.0 and from 3.0 to 5.0.

	Decrease in Phenol Recovery [Percentage points]			
S/F	W/S=0.3 H/F=0.5-5.0	W/S=0.3 H/F=3.0-5.0	W/S=0.7 H/F=0.5-5.0	W/S=0.7 H/F=3.0-5.0
0.5	11.1 (97.4-86.3)	4.2 (90.5-86.3)	10.5 (96.6-86.1)	3.6 (89.8-86.1)
1.0	5.6 (98.0-92.4)	1.5 (92.4-93.9)	6.7 (96.8-90.1)	2.9 (92.9-90.1)
1.5	5.0 (98.5-93.5)	1.1 (94.6-93.5)	6.4 (97.0-90.6)	2.4 (93.0-90.6)
2.0	3.8 (98.6-94.8)	1.0 (95.8-94.8)	5.7 (97.3-91.6)	1.9 (93.5-91.6)
3.0	3.0 (99.1-96.1)	1.0 (97.1-96.1)	4.1 (98.0-93.9)	1.3 (93.9-95.3)

It is interesting to note in Table 5-4 that the decrease in phenol recovery is only in the order of 1.0 percentage point as the hexane to feed ratio is increased from 3.0 to 5.0, except at very low solvent to feed ratios. Therefore, if a significant increase in separation efficiency may be achieved by increasing the hexane to feed ratio, it may be done without incurring any significant loss in phenol recovery, especially at water to solvent ratios smaller than 0.3.

The effect of the water to solvent ratio on the phenol recovery is illustrated for various selected solvent to feed and hexane to feed ratios in Figure 5.4-3.

It is apparent that an increase in the water to solvent ratio without exception leads to a decrease in the phenol recovery for all hexane to feed and solvent to feed ratios. Also, the extent to which the phenol recovery decreases with an increase in water to solvent ratio is dependent on both the hexane to feed and the solvent to feed ratio.

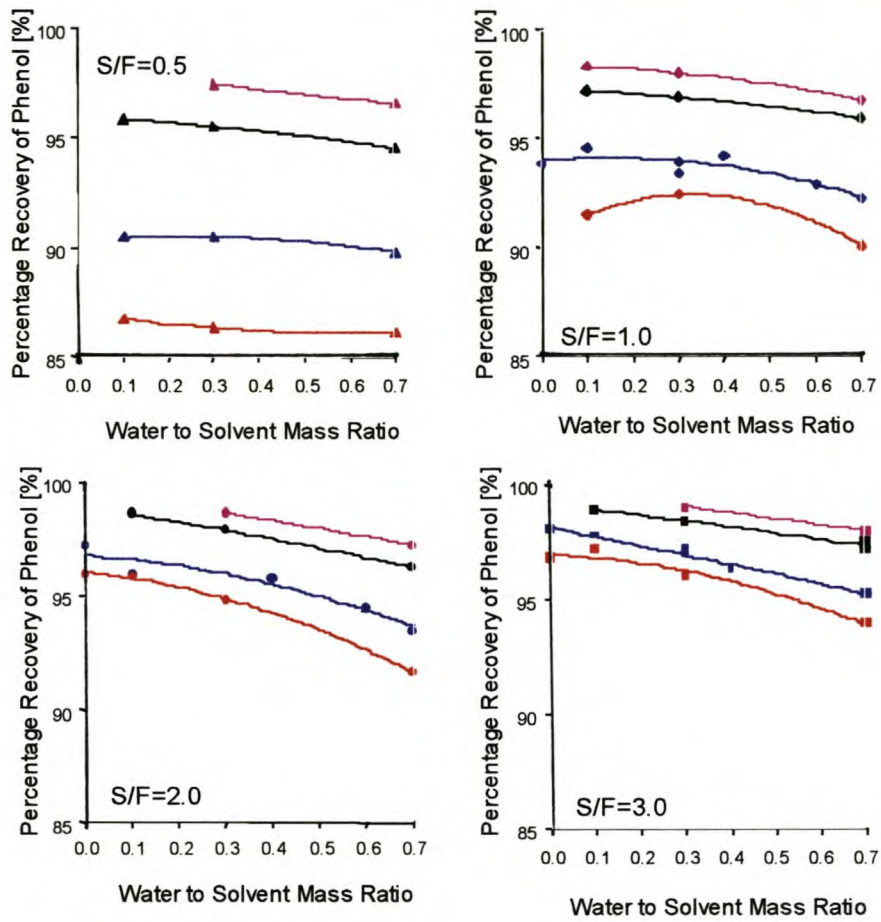


Figure 5.4-3. Effect of water to solvent ratio on phenol recovery at selected solvent to feed and hexane to feed ratios.

▲ S/F=0.5; H/F=0.5 ▲ S/F=0.5; H/F=1.0 ▲ S/F=0.5; H/F=3.0 ▲ S/F=0.5; H/F=5.0
◆ S/F=1.0; H/F=0.5 ◆ S/F=1.0; H/F=1.0 ◆ S/F=1.0; H/F=3.0 ◆ S/F=1.0; H/F=5.0 .
● S/F=2.0; H/F=0.5 ● S/F=2.0; H/F=1.0 ● S/F=2.0; H/F=3.0 ● S/F=2.0; H/F=5.0
■ S/F=3.0; H/F=0.5 ■ S/F=3.0; H/F=1.0 ■ S/F=3.0; H/F=3.0 ■ S/F=3.0; H/F=5.0

From the slope of the lines in Figure 5.4-3 it is clear that the most significant decrease in phenol recovery over a water to solvent ratio range of 0.0 to 0.7 occurs at a solvent to feed ratio of 2.0. The decrease in phenol recovery at the low solvent to feed ratio of 0.5 is negligible. At a solvent to feed ratio of 3.0, the decrease in phenol recovery is significant, but it is less so than at the lower solvent to feed ratio of 2.0.

In order to investigate if this phenomena is limited only to the selected solvent ratios illustrated in Figure 5.4-3, the percentage point decrease in phenol recovery as the water to solvent ratio is increased from 0.1 to 0.7 is listed in Table 5-5 for a wider range of solvent to feed ratios.

Table 5-5. Percentage point decrease in phenol recovery as the water to solvent ratio is increased from 0.1 to 0.7.

	H/F = 1.0	H/F = 3.0	H/F = 5.0
S/F	Decrease in Phenol Recovery [Percentage points]		
0.5	1.3 (95.8-94.5%)	0.6 (90.4-89.8%)	0.7 (86.8-86.1%)
1.0	1.3 (97.2-95.9%)	2.3 (94.2-92.3%)	1.4 (91.5-90.1%)
1.5	2.3 (98.2-95.9%)	2.4 (95.4-93.0%)	3.9 (94.5-90.6%)
2.0	2.3 (98.6-96.3%)	2.4 (95.9-93.5%)	4.2 (95.8-91.6%)
3.0	1.7 (98.9-97.3%)	2.5 (97.8-95.3%)	3.2 (97.8-93.9%)

Table 5-5 shows that at a hexane to feed ratio of 1.0 and 5.0, the most significant decrease in phenol recovery with water to solvent ratio is at solvent to feed ratios of approximately 2.0.

It is also clear from Table 5-5 and Figure 5.4-3 that an increase in the hexane to feed ratio heightens the effect of the water to solvent ratio on phenol recovery.

For example, for a solvent to feed ratio of 2.0 the phenol recovery decreases by 4.4 percentage points (96.0-91.6%) and 3.7 percentage points (97.2-93.5%) at hexane to feed ratios of 5.0 and 3.0 respectively.

The same is true at a solvent to feed ratio of 1.5. The phenol recovery decreases by 4.2 percentage points (94.8-90.6%) and 3.1 percentage points (96.1-93.0%) at hexane to feed ratios of 5.0 and 3.0 respectively.

Unlike the effect of the hexane to feed and solvent to feed ratios, the reason for the effect of the water to solvent ratio on phenol recovery is not immediately apparent. Phenol is soluble in water and, in a ternary system consisting only of hexane, water and phenol, will preferentially dissolve in the water phase. The decrease in phenol recovery with an increase in the water to solvent ratio is therefore not caused by a decrease in the solubility of phenol in the solvent phase. The phenomenon can however be attributed to the fact that an increase in water to solvent ratio increases the polarity of the solvent mixture, which would substantially decrease the solubility of aromatic feed components such as mesitylene and benzonitrile in the solvent mixture. These components would then preferentially dissolve in the hexane phase and could then fulfil an antisolvent function i.e. the ratio of aromatics to phenol in the hexane phase would increase, thereby increasing the relative solubility of phenol in the hexane phase.

This hypothesis was tested by means of two PROII simulations. These simulations were based on a thermodynamic model developed by means of regression of the liquid-

liquid equilibrium data generated with the batch extractions executed on the synthetic phenol feed stream. The development of the model in question is described in Chapter 6. In the first simulation, the liquid-liquid phase split of a ternary mixture of water, hexane and phenol was simulated at 40°C and atmospheric pressure. In the second, a small amount of mesitylene was added to the feed mixture at the same operating conditions. The feed compositions and results are shown in Table 5-6.

Table 5-6. Effect of mesitylene on phenol distribution between water and hexane

	Phenol	Water	Hexane	Mesitylene
Mass in Feed [g]	5	20	20	0
Mass in Aqueous Phase [g]	4.13	19.992	3.9×10^{-3}	0
Mass in Hexane Phase [g]	0.87	8.3×10^{-3}	19.996	0
Mass in Feed [g]	5	20	20	1
Mass in Aqueous Phase [g]	3.63	19.986	2.8×10^{-3}	4.7×10^{-3}
Mass in Hexane Phase [g]	1.37	0.014	19.997	0.9953

From Table 5-6 it can clearly be seen that the amount of phenol that dissolves in the hexane phase increases substantially with the addition of a small amount of mesitylene to the mixture. Therefore, it can be concluded that the decrease in phenol recovery at increased water to solvent ratios can be attributed to the corresponding increase of aromatic feed component concentration in the hexane phase.

The fact that the effect of the water to solvent ratio on phenol recovery increases as the solvent to feed is increased to 2.0 and then decreases with a further increase in solvent to feed ratio can be attributed to the contrasting effects of an increase in water and an increase in triethylene glycol relative to phenol. At a constant water to solvent ratio, an increase in the solvent to feed ratio by definition results in an increase in the water to feed ratio as well. Thus, the ratio of triethylene glycol to feed increases, resulting in a tendency towards an increase in phenol recovery, while at the same time the ratio of water to feed increases, resulting in a tendency towards a decrease in phenol recovery. As the solvent to feed ratio increases from 0.5 to 2.0 the tendency towards a decrease in phenol recovery is more dominant. However, as the solvent to feed ratio is increased further, the ratio of triethylene glycol to phenol is large enough to counteract the effect of the increased effective water to feed concentration.

It was previously noted that an increase in the solvent to feed ratio from 2.0 to 3.0 results in a relatively small increase in phenol recovery. However, as the effect of the water to solvent ratio on phenol recovery is significantly less at a water to solvent ratio of 3.0 than at 2.0, increasing the solvent to feed ratio to 3.0 is justifiable.

5.4.1.2 m-Cresol Recovery

m-Cresol recoveries, m-cresol-pseudocumene, m-cresol-undecane, m-cresol-indene, m-cresol-o-tolunitrile and m-cresol-o-toluidine separation factors, as well as the percentage of feed pseudocumene, undecane, indene, o-tolunitrile and o-toluidine remaining in the extract phase are listed for various solvent to feed, water to solvent and hexane to feed mass ratios in Table 5-7.

Table 5-7. Percentage recovery of m-Cresol, R_1; separation factors β_{ij}; and percentage of feed neutral oils and nitrogen bases remaining in the extract phase, R_2, R_3, R_4, R_5, R_6; for the system m-Cresol (1) + o-Tolunitrile (2) + o-Toluidine (3) + Indene (4) + Pseudocumene (5) + Undecane (6) + Hexane (7) + Water (8) + Triethylene Glycol (9) at various Solvent to Feed, S/F, Hexane to Feed, H/F, and Water to Solvent, W/S, mass ratios. Temperature 40 °C and Pressure101.3 kPa.

Exp.	Mass Ratios			$R_{m\text{-}Cresol}$	Separation Factors					Percentage Recoveries of Nitrogen Bases and Neutral Oils [%]				
ID.	S/F	H/F	W/S	[%]	β_{12}	β_{13}	β_{14}	β_{15}	$\beta_{16}x10^{-2}$	R_2	R_3	R_4	R_5	R_6
c1a	0.5	3.0	0.68	82.4	11.0	4.2	55.2	125.5	464.3	52.8	29.8	7.8	3.6	0.0
c1b	1.0	3.0	0.70	87.6	16.6	5.5	93.0	146.4	418.4	56.2	29.9	7.1	4.6	0.0
c1c	1.5	3.0	0.69	88.5	18.4	5.9	110.8	443.9	262.0	56.4	29.4	6.5	1.7	0.0
c1d	2.1	3.0	0.65	93.6	31.1	7.8	211.5	276.9	202.9	65.3	32.1	6.5	5.0	0.0
c1e	2.9	2.9	0.66	96.1	48.2	10.3	260.1	641.2	156.7	70.6	33.9	8.7	3.7	0.0
c2a	0.5	3.0	0.33	87.0	11.2	5.2	54.3	119.1	9.7	56.3	37.4	10.9	5.3	0.7
c2b	0.9	2.5	0.34	93.3	18.1	7.6	105.4	225.4	46.6	64.6	43.5	11.7	5.8	0.3
c2c	1.5	3.0	0.33	94.6	25.2	7.9	111.7	429.7	119.8	68.9	41.0	13.5	3.9	0.1
c2d	2.1	3.0	0.31	96.2	34.8	9.2	196.2	614.6	15.9	73.4	42.2	11.5	4.0	0.5
c2e	3.0	3.0	0.33	97.7	50.4	13.0	289.7	2148.7	9.0	76.8	46.0	12.9	0.2	0.7
c3a	1.0	3.0	0.34	92.4	19.2	6.3	99.2	300.6	42.8	65.8	38.7	10.9	3.9	0.3
c3b	1.5	3.0	0.55	92.6	22.6	6.8	145.5	372.2	34.8	64.7	35.7	7.9	3.3	0.4
c3c	1.0	0.5	0.64	94.9	15.7	5.1	50.9	127.8	6.6	78.5	54.1	26.7	12.7	1.2
c3d	1.5	0.5	0.67	95.6	18.4	5.2	63.7	184.7	15.9	80.6	54.2	25.5	10.5	0.6
c3e	2.0	0.5	0.75	96.0	19.1	5.6	92.2	277.2	11.0	80.9	55.6	20.6	7.9	0.8
c4a	1.0	4.0	0.67	88.5	20.5	6.3	113.1	250.6	39.1	54.8	27.3	6.4	3.0	0.2
c4b	0.5	4.0	0.69	81.8	12.0	4.8	57.4	129.3	19.1	48.5	27.2	7.3	3.4	0.2
c4c	1.5	4.1	0.65	92.6	33.3	9.4	200.3	726.6	18.6	57.2	27.4	5.9	1.7	0.3
c4d	2.1	4.0	0.64	92.6	33.0	8.3	213.2	895.2	17.6	60.1	27.5	5.6	1.4	0.3
c4e	2.9	4.0	0.66	93.9	39.3	8.4	265.8	1260.6	24.1	64.7	28.2	5.5	1.2	0.2
c5a	0.5	4.1	0.35	86.4	12.4	5.5	56.4	163.7	15.0	53.9	34.0	10.1	3.7	0.4
c5b	1.0	4.0	0.33	91.5	20.6	6.9	115.1	304.5	51.6	60.8	34.4	8.6	3.4	0.2
c5c	1.5	4.0	0.33	93.2	25.8	8.1	143.5	476.3	29.4	62.9	34.7	8.7	2.8	0.2
c5d	2.0	4.1	0.33	95.2	35.4	8.8	197.5	984.5	102.1	69.4	36.1	9.2	2.0	0.1
c5e	3.0	4.0	0.33	97.3	47.1	11.1	332.8	1087.7	169.5	76.2	42.9	9.6	3.2	0.1
c6a	1.0	1.0	0.65	94.4	16.8	5.4	74.7	211.6	32.6	75.6	50.1	18.4	7.4	0.5
c6b	1.0	2.9	0.11	95.0	22.6	7.5	110.1	251.7	23.8	71.4	45.5	14.6	7.0	0.8
c6c	1.5	3.1	0.11	96.4	26.6	7.4	117.2	N/A	11.7	78.4	50.4	18.7	0.0	0.8
c6d	2.0	3.0	0.12	97.3	34.5	8.4	172.9	N/A	27.8	81.3	51.2	17.4	0.0	0.4
c6e	3.0	3.0	0.11	97.4	28.2	6.6	116.7	N/A	12.1	85.1	57.2	24.4	0.0	0.9
c7a	0.5	5.0	0.35	84.8	11.9	6.2	66.9	198.4	18.6	47.2	32.0	7.7	2.7	0.3

Table 5-7 (continued).

Exp.	Mass Ratios			$R_{m\text{-}Cresol}$	Separation Factors					Percentage Recoveries of Nitrogen Bases and Neutral Oils [%]				
ID.	S/F	H/F	W/S	[%]	β_{12}	β_{13}	β_{14}	β_{15}	$\beta_{16}x10^{-2}$	R_2	R_3	R_4	R_5	R_6
c7b	1.0	5.0	0.33	91.4	24.3	7.6	132.9	427.6	89.3	58.2	30.3	7.4	2.4	0.1
c7c	1.5	4.9	0.32	92.8	28.9	8.0	165.4	467.7	16.9	61.5	30.7	7.2	2.7	0.3
c7d	2.0	5.0	0.33	94.3	33.3	8.6	207.6	607.8	35.2	66.0	33.3	7.4	2.7	0.2
c7e	3.0	5.1	0.35	95.3	40.2	9.0	220.2	549.2	32.9	69.3	33.5	8.4	3.6	0.2
c8a	0.5	5.0	0.66	82.4	15.2	6.2	78.3	221.9	25.1	43.2	23.5	5.6	2.1	0.2
c8b	1.0	4.9	0.67	87.3	22.3	7.8	171.5	708.2	49.0	47.0	23.6	3.9	1.0	0.1
c8c	1.5	5.0	0.68	89.5	27.3	7.9	173.7	661.9	44.0	52.0	23.8	4.7	1.3	0.1
c8d	2.0	5.0	0.68	91.5	33.1	8.0	217.0	845.9	65.0	57.3	24.4	4.7	1.2	0.1
c8e	3.0	5.0	0.67	92.8	38.4	8.3	219.6	724.0	40.6	60.9	25.2	5.5	1.7	0.1
c9a	0.5	0.6	0.12	96.4	7.5	4.0	26.5	53.0	2.5	87.2	78.3	50.5	33.8	9.7
c9b	1.0	0.5	0.11	98.4	15.9	6.2	63.7	135.4	11.3	90.9	79.4	49.0	31.2	5.1
c9c	1.5	0.5	0.11	98.9	19.6	6.5	80.8	208.6	7.1	93.0	81.5	51.6	29.2	3.7
c9d	2.0	0.5	0.11	99.1	22.2	6.7	96.0	277.7	8.0	94.3	83.2	53.4	28.4	3.8
c9e	3.0	0.5	0.11	99.5	30.1	7.7	131.9	416.6	9.9	96.0	85.9	58.1	30.5	4.1
c10a	0.5	4.9	0.11	85.6	11.0	5.3	61.0	129.5	13.8	52.8	34.9	8.9	4.4	0.4
c10b	1.0	5.0	0.11	92.3	19.5	7.0	104.2	262.9	21.7	62.9	38.0	10.3	4.3	0.5
c10c	1.5	5.0	0.11	95.6	31.4	9.7	165.3	463.6	11.5	69.1	40.8	11.6	4.5	0.6
c10d	2.0	5.0	0.11	97.0	41.0	10.9	206.9	786.6	22.7	74.8	44.1	13.5	4.0	0.4
c10e	3.0	5.1	0.11	97.8	47.7	12.2	222.6	638.4	12.4	78.6	48.5	16.8	6.6	0.8
c11a	0.5	3.1	0.00	90.2	11.3	5.2	40.9	93.7	4.6	64.0	44.9	18.4	9.0	2.0
c11b	1.5	3.1	0.00	97.3	28.7	9.9	106.9	335.6	24.5	78.6	56.0	25.5	9.8	1.5
c11c	1.0	3.0	0.00	97.6	31.4	10.7	133.9	372.1	6.9	79.0	56.1	23.0	9.7	1.5
c11d	2.0	3.0	0.00	98.2	35.7	10.8	140.4	377.8	4.2	83.2	60.0	27.6	12.4	3.0
c11e	3.0	3.0	0.00	99.0	45.9	12.4	205.6	557.5	5.9	89.3	69.3	33.5	15.7	3.1
c12a	0.5	4.1	0.00	88.2	12.1	5.3	46.5	100.0	5.5	58.5	38.3	13.9	7.0	1.3
c12b	1.0	4.0	0.00	95.2	23.8	8.5	104.5	262.8	23.8	69.8	45.2	15.8	7.0	0.8
c12c	1.5	4.0	0.00	96.9	31.2	9.4	135.3	408.4	13.3	76.9	50.1	18.8	7.1	0.7
c12d	2.0	4.0	0.00	97.5	36.8	10.5	148.9	461.6	10.4	79.1	51.8	21.0	7.9	1.0
c12e	3.0	4.0	0.00	98.6	46.1	12.3	168.4	641.1	10.7	84.9	60.0	29.2	9.8	1.3
c13a	0.5	5.1	0.00	85.7	10.8	5.1	48.4	106.4	5.1	53.7	35.6	11.0	5.3	1.2
c13b	1.0	5.0	0.00	93.7	18.4	6.9	103.3	199.9	11.5	68.3	44.6	12.5	6.9	1.3
c13c	1.5	4.9	0.00	96.5	31.1	9.4	135.4	313.2	4.2	74.2	46.6	16.7	8.0	1.9
c13d	2.0	5.0	0.00	97.5	36.8	10.4	155.2	475.2	5.2	79.1	51.7	20.3	7.7	1.9
c13e	3.0	4.9	0.00	98.2	45.9	11.9	104.7	175.4	0.9	82.4	54.7	34.6	24.0	12.1
c14a	2.5	0.5	0.33	98.8	34.3	7.9	145.6	632.8	233.4	91.4	71.0	36.6	11.7	0.4
c14b	2.5	1.0	0.33	98.6	40.3	10.1	218.3	847.0	263.9	87.1	62.8	23.8	7.4	0.3
c14c	2.5	2.0	0.34	98.1	46.9	11.1	269.4	706.4	72.9	82.0	51.9	15.8	6.7	0.2
c14d	2.5	3.0	0.33	97.6	50.7	13.1	291.3	937.9	47.1	76.0	45.0	12.5	4.2	0.2
c14e	2.6	3.9	0.32	97.0	43.5	10.9	233.2	748.8	26.4	74.9	42.8	12.2	4.2	0.3
c15a	2.5	4.9	0.00	98.1	43.4	11.2	163.2	331.2	10.4	82.2	54.4	24.1	13.5	4.8
c15b	2.5	5.0	0.11	97.4	45.9	12.1	169.7	369.1	27.0	75.6	44.8	18.0	9.2	1.4
c15c	2.6	5.0	0.32	95.2	35.3	8.9	176.4	370.3	20.3	69.2	36.2	10.2	5.1	0.3
c15d	2.5	5.0	0.66	92.0	34.3	8.2	234.1	709.9	21.3	58.2	25.1	4.7	1.6	0.2
c15e	2.5	4.9	0.99	91.2	42.3	9.1	381.0	1607.1	54.5	53.4	19.8	2.7	0.6	0.1

Table 5-7 (continued).

Exp.	Mass Ratios			$R_{m\text{-}Cresol}$	Separation Factors					Percentage Recoveries of Nitrogen Bases and Neutral Oils [%]				
ID.	S/F	H/F	W/S	[%]	β_{12}	β_{13}	β_{14}	β_{15}	$\beta_{16}x10^{-2}$	R_2	R_3	R_4	R_5	R_6
c16a	1.0	4.0	0.11	93.8	24.0	7.5	119.0	317.3	33.6	66.8	38.6	11.2	4.5	0.4
c16b	1.5	4.1	0.11	96.7	37.0	10.7	164.3	577.2	65.6	72.9	43.9	15.0	4.8	0.4
c16c	0.5	4.1	0.11	88.0	12.5	5.6	55.4	139.8	5.4	56.6	37.0	11.7	5.0	0.7
c16d	2.0	4.0	0.11	97.5	42.3	11.1	187.0	721.1	23.6	77.6	47.6	17.0	5.0	0.4
c16e	3.0	4.1	0.11	98.4	56.6	13.6	263.6	903.5	13.6	82.1	52.5	19.2	6.5	0.8
c17a	0.5	3.0	0.11	90.9	12.2	3.9	48.8	123.0	13.5	71.7	44.8	16.9	7.5	0.7
c17b	1.5	3.0	0.11	96.8	28.6	9.6	136.5	353.9	17.7	75.9	51.5	18.2	7.9	1.7
c17c	2.0	3.0	0.11	97.7	35.1	11.0	147.6	365.2	4.2	79.3	54.6	22.2	10.4	2.5
c17d	2.5	3.0	0.11	98.4	47.2	12.0	195.4	533.0	6.0	83.6	56.4	23.8	10.3	2.1
c17e	3.0	3.0	0.11	98.7	54.7	13.4	238.4	490.9	5.1	84.9	57.8	23.9	13.2	2.6
c18a	2.5	4.0	0.00	98.2	37.6	11.4	152.9	351.5	12.8	82.4	58.6	25.8	13.2	4.0
c18b	2.5	4.0	0.11	98.0	46.0	12.2	203.1	464.5	20.4	80.4	52.1	19.7	9.7	2.4
c18c	2.5	3.0	0.00	98.7	39.9	11.9	152.7	368.2	2.3	86.5	65.6	33.2	17.1	6.6
c18d	2.5	4.0	0.66	93.6	38.0	8.4	252.0	822.1	17.4	63.4	27.8	5.5	1.7	0.3
c18e	2.5	3.0	0.66	95.6	45.0	9.5	260.3	942.2	20.9	69.8	32.8	7.8	2.3	0.3
c19a	1.0	0.5	0.33	97.6	18.0	6.1	72.8	122.1	10.7	87.2	69.8	36.3	25.4	3.8
c19b	1.5	0.5	0.34	98.3	24.0	7.6	99.4	267.0	29.0	88.4	70.6	36.8	17.8	2.0
c19c	2.0	0.5	0.33	98.6	30.1	7.7	125.4	370.0	11.1	90.5	70.7	36.7	16.4	1.7
c19d	2.5	0.5	0.11	99.4	29.3	7.1	121.5	457.8	9.8	95.9	85.1	58.1	26.9	3.9
c19e	3.0	0.5	0.35	99.4	44.9	8.3	151.2	626.1	10.3	95.4	79.4	53.3	21.6	3.0
c20a	2.5	0.5	0.66	97.3	28.3	6.6	103.8	188.2	42.8	84.5	55.8	25.7	16.0	0.8
c20b	3.0	0.5	0.66	97.4	29.1	6.7	132.3	554.1	52.1	84.6	55.9	21.8	6.2	0.7
c20c	3.0	1.0	0.34	98.8	46.8	11.9	220.3	748.6	16.8	87.6	64.2	27.6	10.1	1.0
c20d	2.0	1.0	0.33	98.0	29.9	8.2	133.3	490.6	12.2	85.7	62.2	26.9	9.1	1.1
c20e	1.5	1.0	0.34	97.3	24.1	7.9	110.6	336.4	8.3	82.2	60.3	24.9	9.8	1.4
c21a	3.1	5.1	0.33	97.3	66.7	16.3	291.8	820.2	69.3	68.5	34.7	10.9	4.2	0.5
c21b	3.1	5.3	0.33	97.4	62.0	12.0	223.2	514.9	52.6	75.5	37.4	14.3	6.7	0.7
c21c	3.1	5.3	0.33	97.2	63.4	10.9	73.4	507.1	13.3	76.0	35.3	14.4	6.4	0.9
c21d	3.1	4.1	0.34	97.5	59.7	12.0	66.8	726.5	17.8	76.4	39.3	12.6	5.1	0.5
c21e	3.2	4.2	0.34	97.8	56.0	4.6	87.1	728.5	21.0	90.9	44.8	16.3	5.9	0.8
c22a	2.1	4.1	0.33	96.5	50.6	10.9	232.4	665.3	54.0	71.9	35.6	10.7	4.0	0.5
c22b	2.1	4.2	0.34	96.6	52.1	15.9	253.8	578.8	24.6	63.9	35.0	10.0	4.6	1.1
c22c	2.1	5.9	0.33	95.4	47.3	13.7	63.7	454.8	9.2	60.2	30.5	9.3	4.4	0.7
c22d	2.1	5.2	0.34	96.1	52.5	14.5	80.9	483.6	14.1	62.9	31.8	9.6	4.8	0.6
c22e	2.2	5.6	0.33	95.8	47.5	10.3	74.3	467.9	13.6	69.0	32.5	11.4	4.7	0.7

In comparing Table 5-7 to Table 5-2, it can be seen that m-cresol recoveries are lower than the corresponding phenol recoveries. Recoveries lower than 90% are without exception obtained either at the very low solvent to feed ratios of 0.5 or at the very high water to solvent ratio of 0.7. Solvent to feed ratios of 3.0 yield recoveries ranging from 92.8% to 99.5% where the recoveries lower than 95% all correspond to water to solvent ratios of 0.7.

The effect of the solvent to feed ratio on m-cresol recovery at selected constant hexane to feed and water to solvent ratios is shown in Figure 5.4-4.

As with phenol, the recovery of m-cresol increases with an increase in the solvent to feed ratio. The increase is most significant at high hexane to feed ratios.

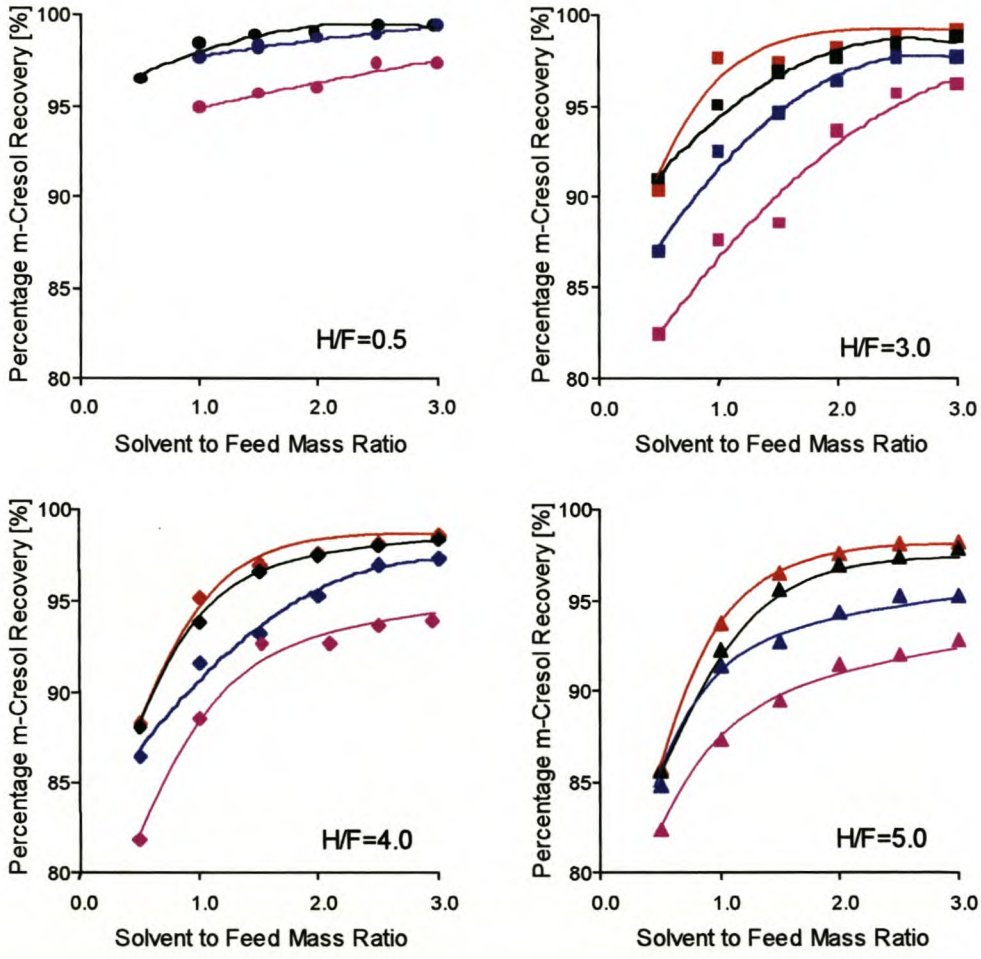


Figure 5.4-4. Effect of Solvent to Feed Ratio on m-Cresol Recovery at Selected Hexane to Feed and Water to Solvent ratios

● H/F=0.5; W/S=0.7 ● H/F=0.5; W/S=0.3 ● H/F=0.5; W/S=0.1
■ H/F=3.0; W/S=0.7 ■ H/F=3.0; W/S=0.3 ■ H/F=3.0; W/S=0.1 ■ H/F=3.0; W/S=0.0
◆ H/F=4.0; W/S=0.7 ◆ H/F=4.0; W/S=0.3 ◆ H/F=4.0; W/S=0.1 ◆ H/F=4.0; W/S=0.0
▲ H/F=5.0; W/S=0.7 ▲ H/F=5.0; W/S=0.3 ▲ H/F=5.0; W/S=0.1 ▲ H/F=5.0; W/S=0.0

The increase in m-cresol recovery is most significant as the solvent to feed ratio is increased from 0.5 to approximately 1.25. As was the case with phenol, the best m-cresol recovery is reached at a solvent to feed ratio of 3.0. A further increase in the solvent to feed ratio cannot be justified in terms of additional m-cresol recovery.

The abovementioned trends, i.e. the initial significant increase in m-cresol recovery as the solvent to feed ratio is increased, followed by a more gradual increase in m-cresol recovery as the solvent to feed ratio is increased further, are analogous to those observed for phenol recovery. As with phenol, the increase in m-cresol recovery with an increase in the solvent to feed ratio can be attributed to the fact that an increase in the solvent to feed ratio results in an increase in the triethylene glycol to m-cresol ratio as well as the triethylene glycol to hexane ratio. As a result, the number of triethylene glycol hydroxyl groups available for the formation of hydrogen bonds as well as the potential for a m-cresol molecule to dissolve in the solvent phase rather than the hexane phase increases. The m-cresol recovery therefore increases until a point is reached where the ratio of hexane to dissolved m-cresol is high enough that a proportionally larger increase in the solvent to feed ratio is required to extract it from the hexane phase. Thus, as was the case with phenol, the increase in m-cresol recovery with an increase in the solvent to feed ratio becomes less significant as the m-cresol recovery becomes very high.

The effect of the water to solvent ratio on m-cresol recovery is illustrated in Figure 5.4-5. As was the case with phenol, the m-cresol recovery decreases with an increase in the water to solvent ratio. However, the decrease in m-cresol recovery is noticeably more significant than the corresponding decrease in phenol recovery.

The reason for the decrease of the m-cresol recovery with an increase in the water to solvent ratio is more apparent than was the case with phenol. m-Cresol and water are immiscible. Therefore, an increase in the water to solvent ratio effectively decreases the solubility of m-cresol in the solvent mixture. As with the phenol feed stream, an increase in the water content of the solvent phase will reduce the solubility of neutral oils such pseudocumene and indene as well as nitrogen bases such as o-tolunitrile in the solvent phase. The aromatic content of the hexane phase will thus be increased, thereby increasing the solubility of m-cresol in the hexane phase. Thus the impact of an increase in the water to solvent ratio will have a dual impact on m-cresol recovery. As such, it is predictable that the decrease in m-cresol recovery for a given increase in the water to solvent ratio will be greater than the corresponding decrease in phenol recovery.

The effect of solvent to feed ratio on the extent to which the m-cresol recovery decreases as the water to solvent ratio is increased from 0.0 to 0.67, is illustrated in Table 5-8.

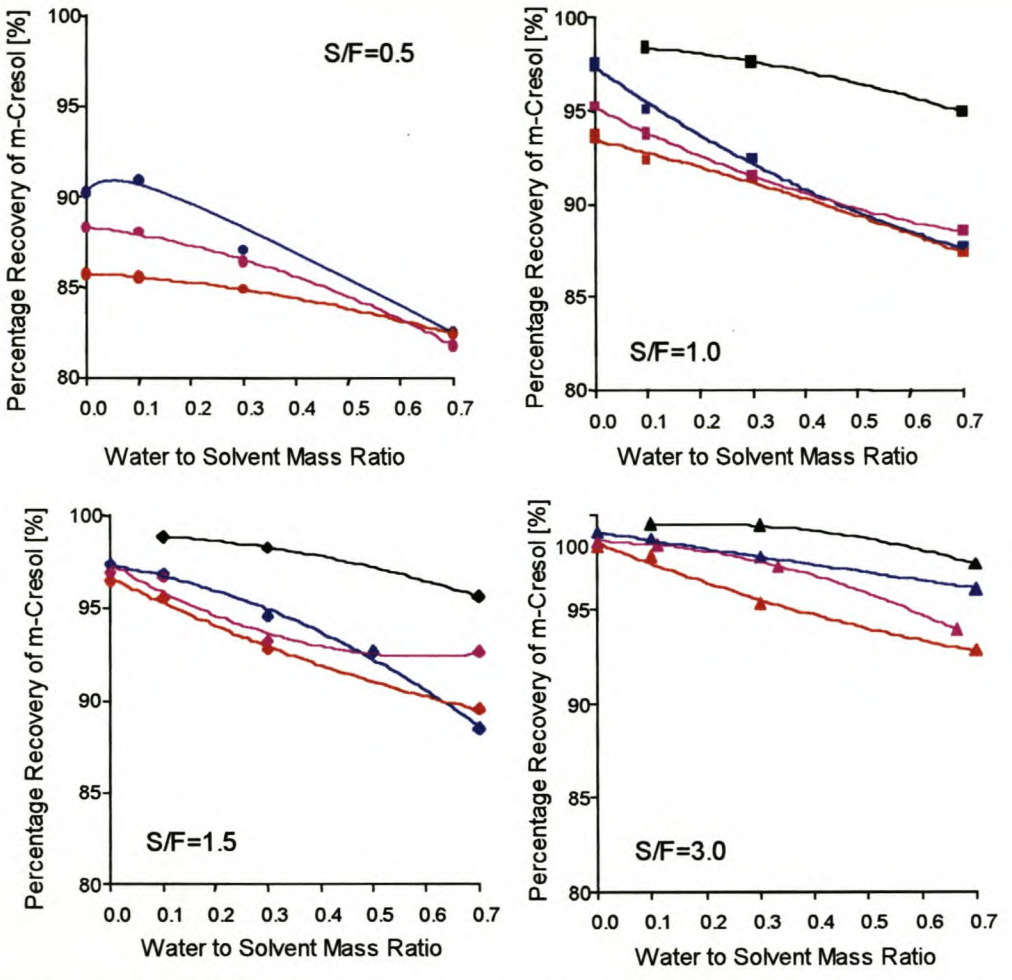


Figure 5.4-5. Effect of water to solvent ratio on m-cresol recovery at selected solvent to feed and hexane to feed ratios.

● S/F=0.5; H/F=5.0 ● S/F=0.5; H/F=3.0 ● S/F=0.5; H/F=1.0
■ S/F=1.0; H/F=5.0 ■ S/F=1.0; H/F=3.0 ■ S/F=1.0; H/F=1.0 ■ S/F=1.0; H/F=0.5
◆ S/F=1.5; H/F=5.0 ◆ S/F=1.5; H/F=3.0 ◆ S/F=1.5; H/F=1.0 ◆ S/F=1.5; H/F=0.5
▲ S/F=3.0; H/F=5.0 ▲ S/F=3.0; H/F=3.0 ▲ S/F=3.0; H/F=1.0 ▲ S/F=3.0; H/F=0.5

Table 5-8. Percentage point decrease in m-cresol recovery as the water to solvent ratio is increased from 0.0 to 0.7.

	H/F = 3.0	H/F = 4.0	H/F = 5.0
S/F	Decrease in Phenol Recovery [Percentage points]		
0.5	7.8 (90.2-82.4)	6.4 (88.2-81.8)	3.3 (85.7-82.4)
1.0	10.0 (97.6-87.6)	6.7 (95.2-88.5)	6.4 (93.7-87.3)
1.5	8.9 (97.3-88.5)	4.3 (96.9-92.6)	7.0 (96.5-89.5)
2.0	4.5 (98.2-93.6)	4.9 (97.5-92.6)	6.1 (97.5-91.5)
2.5	3.1 (98.7-95.6)	4.6 (98.2-93.6)	6.1 (98.1-92.0)
3.0	2.9 (99.0-96.1)	4.7 (98.6-93.9)	5.4 (98.2-92.8)

As was illustrated for the phenol recoveries in Table 5-5, the effect of the water to solvent ratio on the phenolic recovery varies with the solvent to feed ratio. However, in the case of m-cresol, the solvent to feed ratio at which the phenolic recovery is most sensitive to an increase in the water to solvent ratio is 1.0, and not 2.0 as for phenol. E.g. at a hexane to feed ratio of 3.0 and solvent to feed ratio of 1.0, the m-cresol recovery decreases from 97.6% to 87.6% as the water to solvent ratio is increased from 0.0 to 0.67. At the same hexane to feed ratio and a solvent to feed ratio of 3.0, the m-cresol recovery decreases by only 2.9 percentage points, from 99.0% to 96.1%. At a hexane to feed ratio of 5.0, the most significant water to solvent ratio effect is observed at a solvent to feed ratio of 1.5.

As with phenol, the differing sensitivity of the m-cresol recovery to an increase in the water to solvent ratio at various solvent to feed ratios can be attributed to the conflicting effects of the corresponding increase in water and triethylene glycol relative to m-cresol.

m-Cresol recovery is most sensitive to an increase in the water to solvent ratio at a solvent to feed ratio of approximately 1.25. Phenol recovery, on the other hand, is most sensitive to an increase in the water to solvent ratio at a solvent to feed ratio of approximately 2.0. This can be attributed to the difference in the percentage of phenol and m-cresol in their respective feed streams, namely 71.0% and 53.3%. Therefore, at any given solvent to feed ratio, the effective triethylene glycol to m-cresol ratio is higher than the corresponding triethylene glycol to phenol ratio. In fact, at a solvent to feed ratio of 2.0, the molar triethylene glycol to phenol ratio is 1.8, while at a solvent to feed ratio of 1.25 the molar triethylene glycol to m-cresol ratio is 1.7. The types and concentrations of neutral oils and nitrogen bases in the two feed streams also differs. Thus, while the general effect of the solvent to feed, water to solvent and hexane to feed ratio should be similar for the three feed streams investigated, the specific solvent ratios at which changes in trends occur can be expected to differ for each feed stream.

The effect of the hexane to feed ratio on m-cresol recovery is illustrated in Figure 5.4-6. Both Figure 5.4-6 and Table 5-9 show that the effect of the hexane to feed ratio on m-cresol recovery is greater at higher water to solvent ratios and low solvent to feed ratios.

Table 5-9 shows that, at a water to solvent ratio of 0.1 and a solvent to feed ratio of 3.0, the hexane to feed ratio may be increased from 0.5 to 5.0 with only a 1.6 percentage point decrease in m-cresol recovery from 99.5% to 97.8%. Thus, at low water to solvent ratios, an increase in the hexane to feed ratio from 3.0 to 5.0 would be justified if this increase improves separation efficiency.

Table 5-9. Percentage point decrease in m-cresol recovery as the hexane to feed ratio is increased from 0.5 to 5.0 and from 3.0 to 5.0.

	Decrease in Phenol Recovery [Percentage points]					
S/F	W/S=0.1 H/F=0.5-5.0	W/S=0.1 H/F=3.0-5.0	W/S=0.3 H/F=0.5-5.0	W/S=0.3 H/F=3.0-5.0	W/S=0.67 H/F=0.5-5.0	W/S=0.7 H/F=0.5-5.0
1.0	6.1	2.7	6.3	1.0	7.6	0.3
1.5	3.3	1.2	5.5	1.8	6.1	-
2.0	2.1	0.7	4.3	1.9	4.5	2.2
2.5	2.0	1.0	3.6	2.4	5.3	3.7
3.0	1.6	0.9	4.1	2.4	4.6	3.3

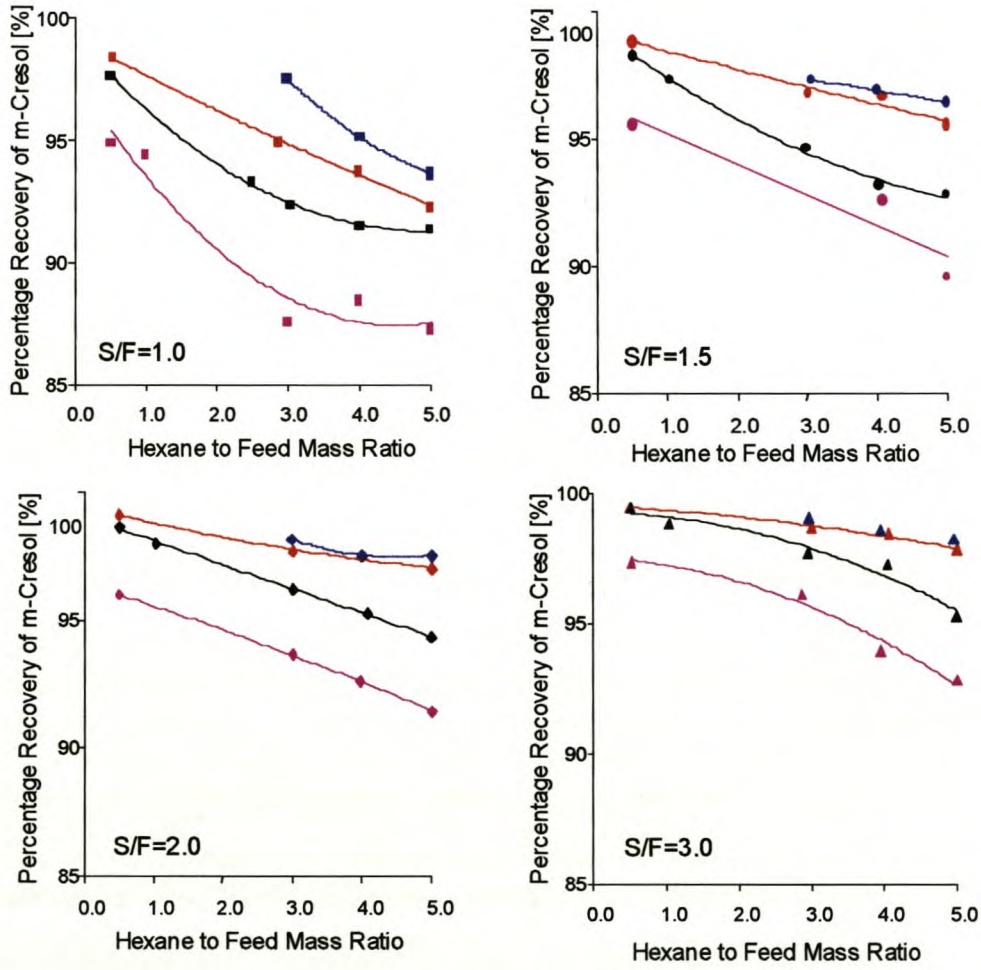


Figure 5.4-6. Effect of hexane to feed ratio on the m-cresol recovery at selected solvent to feed and water to solvent ratios.

■ S/F=1.0; W/S=0.7 ■ S/F=1.0; W/S=0.3 ■ S/F=1.0; W/S=0.1 ■ S/F=1.0; W/S=0.0
● S/F=1.5; W/S=0.7 ● S/F=1.5; W/S=0.3 ● S/F=1.5; W/S=0.1 ● S/F=1.5; W/S=0.0
◆ S/F=2.0; W/S=0.7 ◆ S/F=2.0; W/S=0.3 ◆ S/F=2.0; W/S=0.1 ◆ S/F=2.0; W/S=0.0
▲ S/F=3.0; W/S=0.7 ▲ S/F=3.0; W/S=0.3 ▲ S/F=3.0; W/S=0.1 ▲ S/F=3.0; W/S=0.0

5.4.1.3 Xylenol Recovery

2,4-, 3,5- and 3,4-Xylenol recoveries, xylenol-dodecane, xylenol-indane, and xylenol-naphthalene separation factors, as well as the percentage of dodecane, indane and naphthalene remaining in the extract phase are listed for various solvent to feed, water to solvent and hexane to feed mass ratios in Table 5-10.

In comparing Table 5-10 to Table 5-7 and Table 5-2 it is apparent that the recoveries of the xylenol isomers are markedly more sensitive to the solvent to feed, hexane to feed and especially water to solvent ratios than those of m-cresol and phenol .

Despite this fact, recovery values of greater than 90% are achieved in many cases. 3,4- and 3,5-xylenol recoveries in excess of 95% can be achieved. For example, recoveries of 96.5% and 96.0% are achieved for 3,5- and 3,4-xylenol respectively at a relatively high hexane to feed ratio of 4.0. 2,4-Xylenol recoveries in excess of 95% are achieved only at hexane to feed and water to solvent ratios smaller than 3.0 and 0.1 respectively.

The effect of the solvent to feed ratio on xylenol recovery is illustrated in Figure 5.4-7.

Table 5-10. Percentage recovery of 2,4-, 3,5- and 3,4-Xylenol, R_1, R_2, R_3; separation factors β_{ij}; and percentage of feed neutral oils remaining in the extract phase, R_4, R_5, R_6; for the system 2,4-Xylenol (1) + 3,5-Xylenol (2) + 3,4-Xylenol (3) + Indane (4) + Dodecane (5) + Naphthalene (6) + Hexane (7) + Water (8) + Triethylene Glycol (9) at various Solvent to Feed, S/F, Hexane to Feed, H/F, and Water to Solvent, W/S, mass ratios. Temperature 40 °C and Pressure101.3 kPa.

Exp.	Solvent Mass Ratios			Percentage Xylenol Recoveries [%]			Separation Factors			Percentage Neutral Oils Remaining in Extract Phase		
ID.	S/F	H/F	W/S	R_1	R_2	R_3	$\beta_{123,4}$	$\beta_{123,5}$ x10^{-2}	$\beta_{123,6}$	R_4	R_5	R_6
x1a	0.5	1.0	0.67	75.2	80.6	82.3	77.4	9.0	36.3	4.5	0.4	9.1
x1b	1.0	1.0	0.67	80.6	85.2	87.6	133.3	6.2	62.8	3.7	0.8	7.5
x1c	1.5	1.0	0.66	84.7	90.3	89.9	221.6	10.2	89.0	3.0	0.7	7.2
x1d	2.0	1.0	0.67	86.0	90.5	92.2	273.1	103.0	97.8	2.8	0.1	7.4
x1e	3.0	1.0	0.68	89.1	92.8	93.8	684.8	80.8	113.2	1.5	0.1	8.4
x2a	0.5	5.0	0.67	53.1	64.2	65.8	180.8	19.7	70.3	0.8	0.1	2.0
x2b	1.0	5.0	0.66	63.9	73.8	76.0	164.1	2.3	96.6	1.4	1.0	2.3
x2c	1.5	5.0	0.67	69.5	79.0	81.8	1036.6	19.5	143.2	0.3	0.2	2.0
x2d	2.0	4.9	0.67	73.7	82.8	85.8	386.0	38.4	169.4	1.0	0.1	2.2
x2e	3.0	5.0	0.66	79.5	86.2	87.0	496.3	22.7	154.2	1.0	0.2	3.1
x3a	0.5	3.0	0.67	63.7	71.3	73.8	125.2	21.6	52.4	1.7	0.1	3.9
x3b	1.0	3.0	0.67	73.0	74.5	81.9	265.8	126.6	87.3	1.2	0.0	3.4
x3c	1.5	3.0	0.66	77.5	84.8	87.2	512.1	22.4	120.9	0.9	0.2	3.6
x3d	2.0	3.0	0.67	80.4	87.0	88.9	349.0	17.8	127.6	1.5	0.3	4.0
x3e	3.0	3.0	0.66	84.5	90.2	89.5	575.9	30.3	124.8	1.2	0.2	5.2
x4a	0.5	3.9	1.01	48.5	57.8	62.2	168.3	24.3	65.6	0.7	0.0	1.8
x4b	1.0	4.0	0.67	70.8	79.5	82.2	2950.2	27.8	110.4	0.1	0.1	2.8
x4c	1.5	3.9	0.67	74.6	82.9	85.4	1968.6	17.8	124.7	0.2	0.2	3.0
x4d	2.0	4.0	0.67	78.2	86.0	87.8	473.6	95.4	142.2	1.0	0.0	3.2
x4e	2.9	3.9	0.60	80.6	86.5	88.2	386.6	37.0	143.9	1.3	0.1	3.5
x5a	0.5	4.0	0.66	62.3	71.3	75.3	184.7	28.3	67.8	1.1	0.1	3.0
x5b	1.0	4.0	0.33	81.4	88.0	84.7	309.2	104.3	90.4	1.7	0.0	5.4
x5c	1.5	4.0	0.33	85.3	91.1	83.7	351.4	126.7	93.7	1.8	0.0	6.3
x5d	2.0	4.0	0.33	87.9	92.1	93.4	754.2	125.2	113.6	1.2	0.1	7.6
x5e	3.0	4.0	0.33	90.8	93.9	94.6	407.9	166.7	144.4	2.9	0.1	7.9
x6a	1.0	3.0	0.34	82.0	89.9	89.8	274.3	24.9	95.3	2.2	0.2	6.0
x6b	0.5	3.0	0.33	77.9	85.8	86.7	160.5	63.6	64.4	2.8	0.1	6.7
x6c	1.5	3.0	0.33	87.6	91.3	92.9	343.5	32.7	101.3	2.5	0.3	8.1
x6d	2.0	3.0	0.33	89.4	93.5	93.0	391.9	235.6	103.2	2.7	0.0	9.4
x6e	3.0	3.0	0.33	90.6	93.9	94.0	284.8	121.7	103.5	4.0	0.1	10.4
x7a	0.5	5.0	0.34	67.8	76.4	79.9	134.4	8.3	67.4	2.0	0.3	3.9
x7b	1.6	4.9	0.20	85.9	90.4	91.6	273.9	84.6	88.8	2.7	0.1	8.0
x7c	1.5	5.0	0.34	81.6	87.6	89.5	300.7	46.4	107.4	1.9	0.1	5.0
x7d	3.0	4.0	0.66	82.0	88.5	90.0	377.8	16.7	158.1	1.6	0.4	3.6
x7e	3.0	4.9	0.33	89.4	92.8	92.5	400.0	59.1	128.2	2.5	0.2	7.3

Table 5-10. (continued)

Exp.	Solvent Mass Ratios			Percentage Xylenol Recoveries [%]			Separation Factors			Percentage Neutral Oils Remaining in Extract Phase		
ID.	S/F	H/F	W/S	R_1	R_2	R_3	$\beta_{123,4}$	$\beta_{123,5}$ x10^{-2}	$\beta_{123,6}$	R_4	R_5	R_6
x8a	0.5	3.9	0.33	72.3	80.3	82.4	174.7	44.9	62.5	1.9	0.1	5.0
x8b	1.0	5.0	0.34	75.9	83.7	84.4	265.4	18.1	84.3	1.5	0.2	4.5
x8c	1.5	1.0	0.33	92.6	95.2	95.7	281.5	56.0	82.6	5.3	0.3	16.1
x8d	2.0	5.0	0.34	85.9	91.2	91.5	266.3	7.9	124.9	2.8	1.0	5.9
x8e	2.9	1.0	0.33	95.3	97.1	97.4	348.7	632.8	99.7	6.9	0.0	20.5
x9a	0.5	5.0	0.14	70.7	78.7	81.4	137.2	10.9	49.7	2.2	0.3	5.8
x9b	1.0	5.0	0.12	82.5	86.5	88.7	153.0	22.6	62.4	3.6	0.3	8.4
x9c	1.5	5.0	0.11	89.1	91.9	91.5	135.5	30.9	74.6	6.5	0.3	11.2
x9d	2.0	5.0	0.11	89.3	92.7	93.8	146.9	26.6	70.6	6.7	0.4	12.9
x9e	3.0	5.0	0.11	94.7	97.3	94.6	225.1	42.1	103.4	8.3	0.5	16.4
x10a	0.5	3.8	0.20	79.7	83.0	84.4	166.5	64.5	62.5	2.6	0.1	6.7
x10b	1.0	4.0	0.11	82.5	88.4	89.6	182.5	15.7	57.9	3.2	0.4	9.4
x10c	1.5	3.9	0.11	89.7	92.5	94.6	218.4	59.2	73.4	4.8	0.2	13.0
x10d	2.1	3.9	0.11	91.5	93.7	94.6	229.0	44.0	69.2	5.4	0.3	15.8
x10e	2.9	3.9	0.11	94.0	96.5	96.0	290.6	20.4	80.1	6.4	1.0	19.8
x11a	0.5	3.0	0.11	77.7	85.3	85.1	102.6	10.6	37.2	4.1	0.4	10.5
x11c	1.5	3.0	0.11	92.5	95.4	95.0	258.4	20.7	76.9	5.6	0.7	16.5
x11d	2.0	3.0	0.11	92.1	94.6	95.3	185.2	45.9	65.1	7.3	0.3	18.2
x11e	3.0	3.0	0.11	96.0	97.5	97.6	339.0	191.1	101.0	8.2	0.2	23.0
x12a	0.5	4.0	0.12	79.4	85.0	87.0	147.2	29.9	55.7	3.1	0.2	7.9
x12b	1.0	4.0	1.00	55.4	65.4	70.0	231.8	8.4	92.0	0.7	0.2	1.7
x12c	1.5	4.1	1.00	58.9	67.3	71.3	287.1	7.4	110.7	0.6	0.2	1.6
x12d	2.0	4.1	1.00	66.4	76.1	79.7	105.6	2.0	136.9	2.4	1.3	1.9
x12e	3.0	4.1	1.00	73.1	82.5	84.6	429.8	32.9	170.3	0.8	0.1	2.1
x13a	0.5	2.0	0.33	81.4	86.6	87.6	134.8	28.1	51.3	3.8	0.2	9.4
x13b	1.0	2.0	0.33	87.9	91.8	92.7	251.8	77.6	83.0	3.5	0.1	9.8
x13c	1.5	2.0	0.33	89.8	92.7	93.5	310.0	43.8	94.9	3.4	0.2	10.2
x13d	2.0	2.1	0.33	91.2	94.5	95.6	380.8	69.4	91.9	3.4	0.2	12.9
x13e	3.0	2.0	0.33	94.3	96.4	96.8	433.6	18.0	119.7	4.6	1.2	15.0
x14a	0.5	2.0	0.11	85.1	89.2	90.2	100.1	15.7	38.0	6.5	0.4	15.5
x14b	1.0	2.3	0.00	92.3	94.5	95.0	-	19.8	44.3	0.0	0.7	24.5
x14c	1.6	3.2	0.00	94.3	96.2	96.4	-	27.4	54.2	0.0	0.7	27.2
x14d	2.1	3.2	0.00	96.1	97.3	98.2	-	42.2	69.1	0.0	0.8	31.6
x14e	3.1	2.1	0.00	98.1	98.7	98.8	-	40.5	69.9	0.0	1.5	47.0
x15a	1.0	2.9	0.10	91.5	94.8	95.6	215.9	103.9	66.7	6.1	0.1	17.4
x15b	1.0	2.0	0.11	92.8	95.2	95.6	278.3	51.5	64.8	5.4	0.3	19.7
x15c	1.5	2.0	0.11	94.8	96.5	95.8	284.3	76.6	61.7	6.9	0.3	25.5
x15d	2.0	2.0	0.11	96.2	97.7	97.2	311.7	74.9	73.6	8.9	0.4	29.3
x15e	3.1	2.1	0.11	97.1	98.4	98.4	372.3	227.9	91.3	10.4	0.2	32.2
x16a	0.5	2.0	0.70	70.5	78.5	81.4	126.4	20.9	57.5	2.4	0.1	5.0
x16b	1.0	2.1	0.66	74.7	84.6	86.5	233.0	87.7	83.9	1.7	0.0	4.6
x16c	1.5	2.0	0.66	81.1	87.9	89.4	355.5	90.6	114.7	1.6	0.1	4.7
x16d	1.9	1.9	0.68	81.6	83.9	88.5	54.2	103.5	94.1	8.7	0.0	5.2
x16e	3.0	2.0	0.68	82.1	87.2	92.6	49.7	79.5	135.5	11.0	0.1	4.3

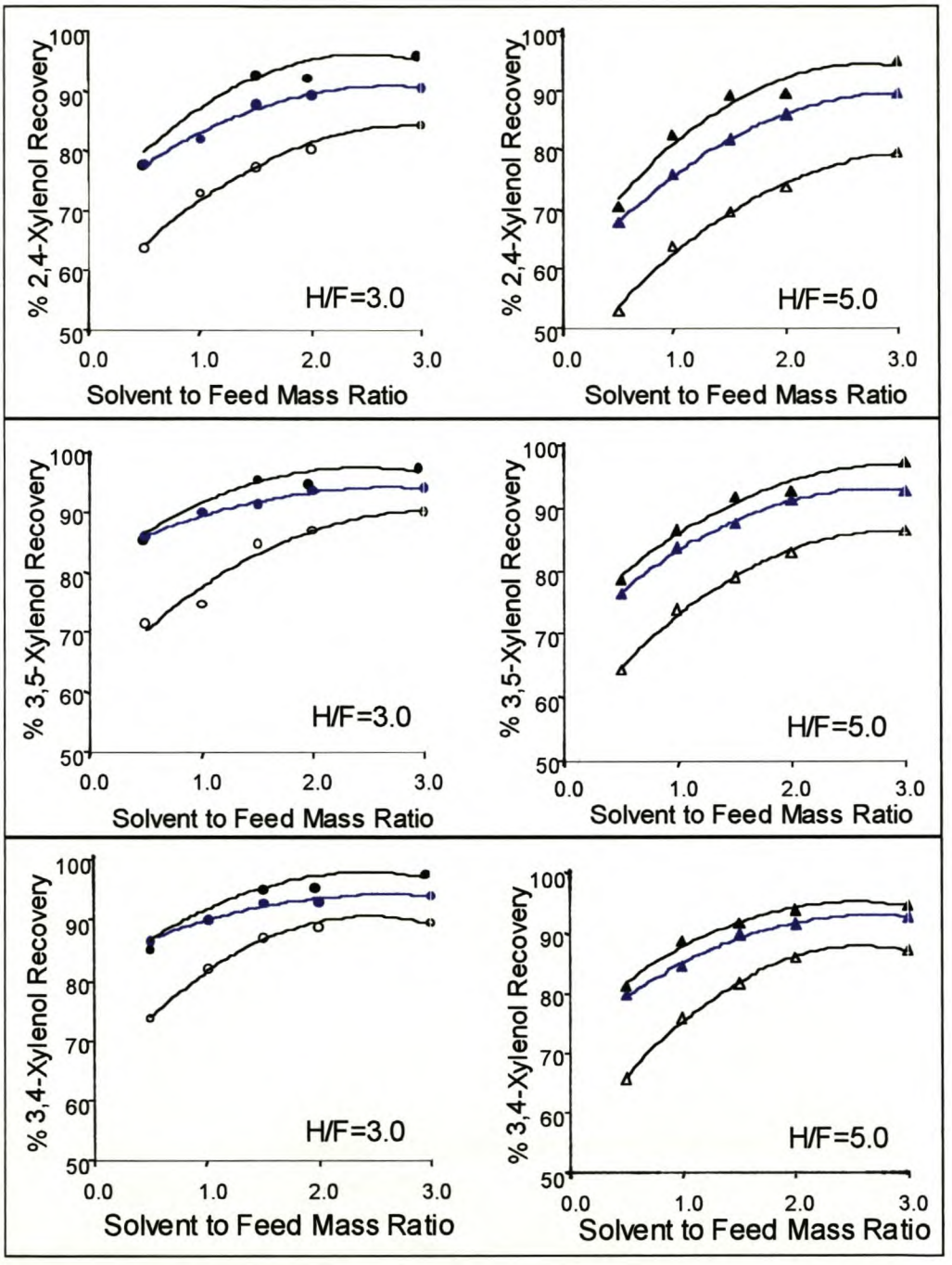


Figure 5.4-7. Effect of solvent to feed ratio on 2,4-, 3,4- and 3,5- xylenol recoveries at various selected hexane to feed and water to solvent ratios

● H/F=3.0; W/S=0.1 ● H/F=3.0; W/S=0.3 O H/F=3.0; W/S=0.67

▲ H/F=5.0; W/S=0.1 ▲ H/F=5.0; W/S=0.3 △ H/F=5.0; W/S=0.67

As with phenol and m-cresol, the recoveries of all three xylenol isomers increase with an increase in solvent to feed ratio. Also, as with phenol and m-cresol, an initial increase in the solvent to feed ratio leads to a significant increase in the xylenol recovery until a point is reached where a further increase in the solvent to feed ratio leads to a more gradual increase in xylenol recovery. The increase in xylenol recovery over selected solvent intervals is illustrated in Table 5-11.

Table 5-11. Increase in 2,4- 3,4- and 3,5-xylenol percentage recoveries as the solvent to feed ratio is increased over selected intervals at a constant hexane to feed ratio of 5.0 and water to solvent ratio of 0.3.

	Increase in Xylenol Recovery [Percentage points]		
Interval over which S/F is increased	2,4-Xylenol	3,5-Xylenol	3,4-Xylenol
0.5 - 1.0	8.1 (67.8-75.9)	4.5 (79.9-84.4)	7.3 (76.4-83.7)
1.0 - 2.0	9.9 (75.9-85.9)	7.1 (84.4-91.5)	7.5 (83.7-91.2)
2.0 - 3.0	3.6 (85.9-89.5)	1.0 (91.5-92.5)	1.6 (91.2-92.8)

It is clear that the increase in recovery of xylenol with an increase of the solvent to feed ratio from 2.0 to 3.0 is much lower than that achieved by increasing the solvent to feed ratio from 1.0 to 2.0. This can be explained by the fact that the percentage of xylenol isomers the xylenol feed stream is only 26.7%.

The effective triethylene glycol to xylenol mass ratio is therefore 7.5 and 11.25 at solvent to feed ratios of 2.0 and 3.0 respectively. This effectively means that the number of hydroxyl groups required for hydrogen bonding is already sufficient to accommodate all the xylenol molecules in the feed at lower solvent to feed ratios. A further increase in the solvent to feed ratio will thus not have a great impact on xylenol recovery.

The fact that the xylenol content of the xylenol feed stream is significantly lower than the phenol and m-cresol contents of the phenol and m-cresol feed streams reflects the reality of an industrial feed stream where the xylenol isomer content is significantly lower than the phenol and cresol isomer content.

From extrapolation of the values in Table 5-12 it can be concluded that the additional xylenol recovery that may be achieved if the solvent to feed ratio is increased beyond a value of 3.0, will be negligible for both 3,5- and 3,4-xylenol. Figure 5.3-7 shows that this trend is true for all three xylenol isomers at most water to solvent and hexane to feed ratios.

The effect of water to solvent ratio on xylenol recovery is illustrated in Figure 5.4-8. It is apparent that the water to solvent ratio leads to an even more significant decrease in xylenol recovery than was the case for m-cresol. This can be attributed to the very low solubility of the xylenol isomers in water.

The significant effect of the water to solvent ratio on xylenol recovery is confirmed in the fact that all of the extractions in which xylenol recoveries are greater than 95% are achieved for water to solvent ratios of 0.3 or less. In contrast, for all three xylenol

isomers, recoveries lower than 70% are all achieved at water to solvent ratios greater than 0.6. The one exception is an extraction in which the recovery of 2,4-xylenol is 67.8% at a water to feed ratio of 0.3. This exception is attributed to the very low solvent to feed ratio of 0.5 and high hexane ratio of 5.0.

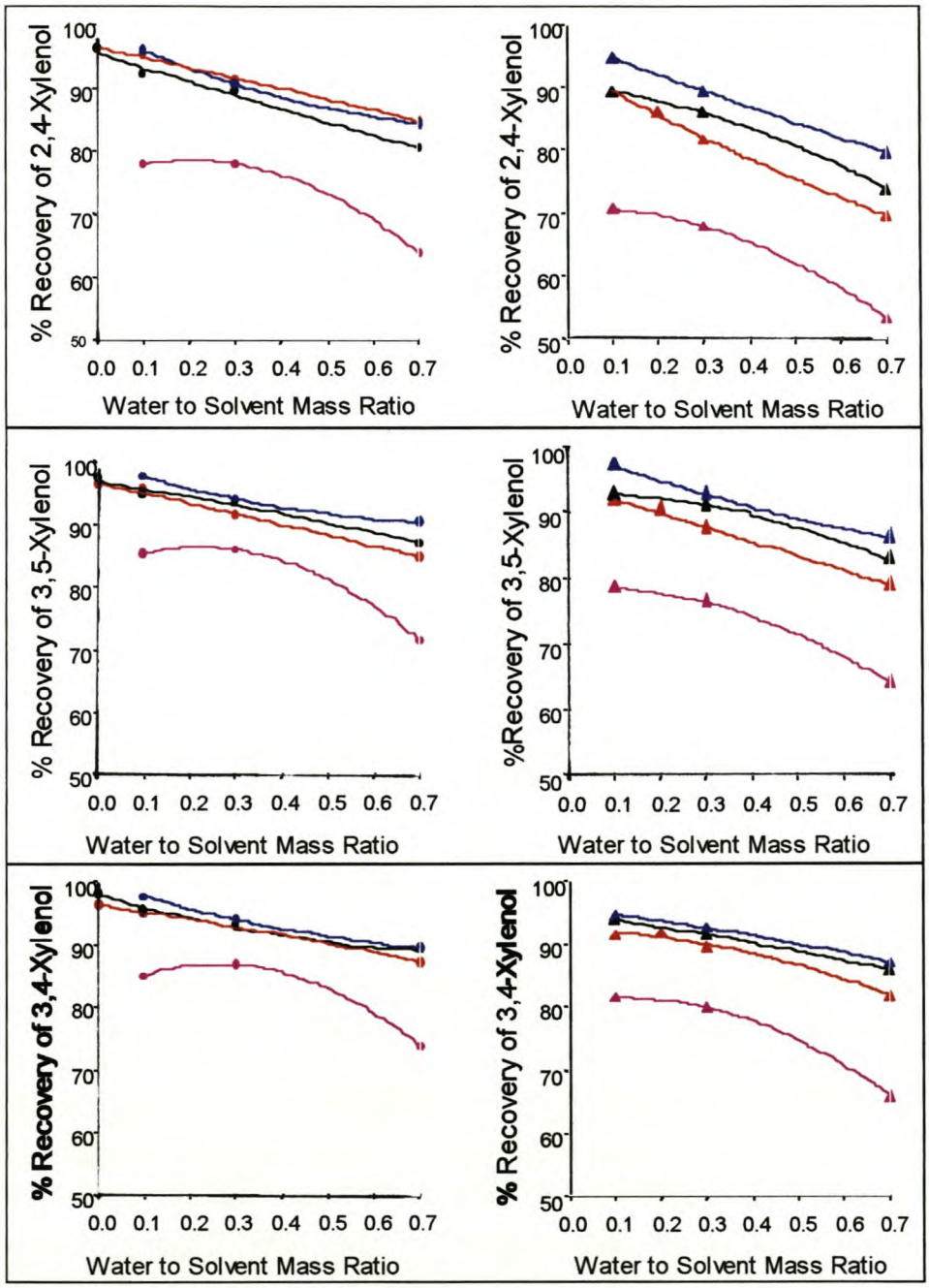


Figure 5.4-8. Effect of water to solvent ratio on 2,4-, 3,4- and 3,5- xylenol recoveries at various selected hexane to feed and water to solvent ratios

● S/F=3.0; H/F=3.0 ● S/F=2.0; H/F=3.0 ● S/F=1.5; H/F=3.0 ● S/F=0.5; H/F=3.0
▲ S/F=3.0; H/F=5.0 ▲ S/F=2.0; H/F=5.0 ▲ S/F=1.5; H/F=5.0 ▲ S/F=0.5; H/F=5.0

From Figure 5.4-8 it can be concluded that a water to solvent ratio greater than 0.3 is extremely detrimental to xylenol recovery at all solvent to feed and hexane to feed ratios.

Form Figure 5.4-9 it can be seen that, as with phenol and m-cresol, an increase in the hexane to feed ratio leads to a decrease in the recovery of all three xylenol isomers. This effect is most significant for the 2,4-xylenol isomer

As with the increase in water to solvent ratio, the increase in the hexane to feed ratio has a more significant effect on xylenol recovery than on phenol and m-cresol recovery.

The fact that xylenol recovery is markedly more sensitive to an increase in water to solvent and hexane to feed ratio than phenol or m-cresol recovery can be attributed to the fact that the xylenol isomers have a lower tendency to form hydrogen bonds with the solvent molecules than are m-cresol and phenol molecules. The comparative tendency to form hydrogen bonds is described in more detail in a subsequent section. As the xylenol molecules are not as effectively held in the solvent phase as are the phenol and m-cresol molecules, these molecules will more freely move from the solvent to phase to the hexane phase. An increase in the water to solvent ratio will therefore have a greater effect on xylenol recovery.

Another factor to be investigated is the effective hexane to xylenol ratio. The effective hexane to xylenol ratios are much higher than the corresponding hexane to phenol and hexane to m-cresol ratios at a given hexane to feed ratio. Thus, while hexane to feed ratios of 3.0 and 5.0 translate to hexane to phenol ratios of 4.2 and 7.0 and hexane to m-cresol ratios of 5.6 and 9.4, the corresponding hexane to xylenol ratios are 11.25 and 18.75. It must however be kept in mind that the effective triethylene glycol to xylenol ratio is also much higher than the corresponding triethylene glycol to phenol and triethylene glycol to m-cresol ratios. The actual ratio of hexane to triethylene glycol is obviously identical at corresponding solvent ratios for all three feed streams. The relative strengths of the conflicting driving forces for a phenolic compound to dissolve in either the hexane or triethylene glycol phase are therefore the same. However, the ratio of dodecane to the combined xylenol isomers in the xylenol feed stream is 1.0, while the ratio of undecane to m-cresol in the m-cresol feed stream is 0.125. Undecane and dodecane are homologues of hexane and can be expected to fulfil an antisolvent function analogous to that of hexane.

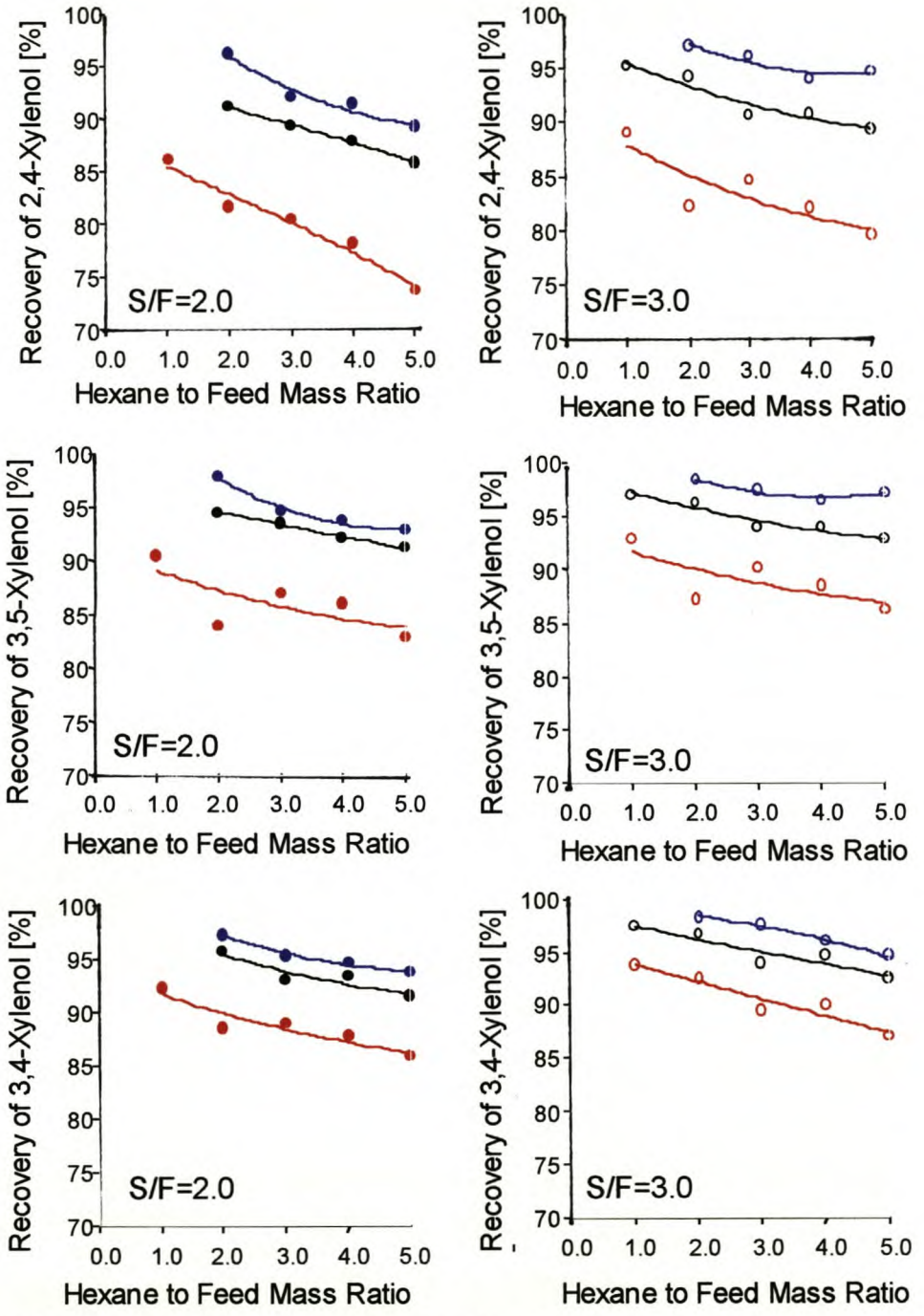


Figure 5.4-9. Effect of hexane to feed ratio on 2,4-, 3,4- and 3,5- xylenol recoveries at various selected solvent to feed and water to solvent ratios

● S/F=2.0; W/S=0.1 ● S/F=2.0; W/S=0.3 ● S/F=2.0; W/S=0.67
O S/F=3.0; W/S=0.1 O S/F=3.0; W/S=0.3 O S/F=3.0; W/S=0.67

It is apparent in Figure 5.4-7, Figure 5.4-8 and Figure 5.4-9 that the recovery of the 2,4-xylenol isomer is significantly inferior to those of the 3,5 and 3,4-xylenol isomers at all solvent ratios. This is attributed to the difference in the relative position on the aromatic ring of the hydroxyl and two methyl functional groups in each of the xylenol isomers. In the case of 2,4-xylenol, one of the methyl functional groups is attached to the aromatic ring at a carbon atom adjacent to that at which the hydroxyl group is attached. As a

result the hydroxyl group is sterically hindered in forming a hydrogen bond with one of the hydroxyl functional groups of the triethylene glycol solvent. In the case of 3,5- and 3,4-xylenol, neither of the two methyl groups is attached to the aromatic ring at carbon atoms adjacent to that at which the hydroxyl group is attached. The measure of steric hindrance offered towards hydrogen bonding between 3,5- and 3,4-xylenol isomers and the solvent is thus considerably less than in the case of the 2,4-xylenol isomer. The affinity of the 2,4-xylenol isomer to the solvent, and therefore the recovery of the 2,4-xylenol isomer, can thus be expected to be lower than that of the other two isomers investigated. With single exceptions, the recovery of 3,4-xylenol is superior to that of 3,5-xylenol over the whole range of solvent ratios tested.

5.4.1.4 Comparison of Recoveries of Phenolic Homologues

The comparative recovery of the phenolic compounds is best illustrated in Figure 5.4-10.

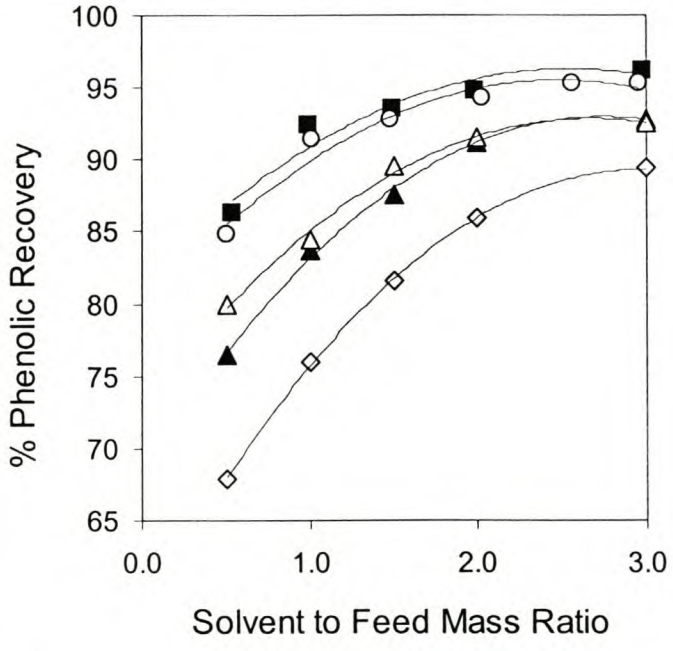


Figure 5.4-10. Effect of the solvent to feed mass ratio on the percentage recovery of phenolic compounds at a constant water to triethylene glycol mass ratio of 0.3 and a constant hexane to feed mass ratio of 5.0.

Phenol O m-Cresol ◇ 2,4-Xylenol 3,5-Xylenol △3,4-Xylenol

It is clear from Figure 5.4-10 that the recovery of the phenolic compounds decreases as the number of methyl groups in the phenolic molecule increases. The recovery also decreases as the number of carbon atoms between the methyl groups and the phenolic

hydroxyl group on the aromatic ring decreases, i.e. as the potential for steric hindrance between the methyl groups and hydroxyl groups increases.

As has been discussed, while the effective solvent to phenol, m-cresol and xylenol and hexane to phenol, m-cresol and xylenol ratios differ, the ratio of triethylene glycol to hexane to water is the same for all three feed streams at corresponding hexane to feed and solvent to feed ratio.

There must therefore be an alternative reason for the decreasing recovery in phenolic recovery with an increase in the homologous series. This reason is twofold: the possibility of shielding of the phenolic hydroxyl group increases and the size of the phenolic molecules increases as the number of methyl groups on the aromatic ring increases. Also, the solubility of the phenolic molecules in water decrease with an increase in the homologous series.

Phenolic molecules are relatively large molecules. The smaller phenol molecules can obviously be accommodated much more easily by the triethylene glycol molecule than can the larger m-cresol or xylenol molecules. The phenol molecule can also approach the hydroxyl groups of the triethylene glycol molecule from any angle as it has no methyl group to shield its hydroxyl group from the hydroxyl groups of the triethylene glycol molecule. While the m-cresol molecule can easily be accommodated by the triethylene glycol molecule, it must be correctly aligned in order to form hydrogen bonds. Thus the phenol molecule will be more prone to the formation of hydrogen bonds than m-cresol. Hydrogen bonds exist in a state of dynamic equilibrium, rapidly forming and breaking under most normal conditions [85]. If the hydrogen bond between a phenolic molecule and a specific solvent hydroxyl group is broken, more alternative hydroxyl groups will be correctly aligned for the speedy formation of another hydrogen bond than will be the case for the m-cresol molecule. The m-cresol molecule would therefore be exposed to the possibility of dissolving in the hexane phase for a longer interval than would the phenol molecule. The xylenol molecules are even less likely to be correctly aligned for the formation of hydrogen bonds than the m-cresol molecules. Due to their extra methyl group, they are also more susceptible to steric hindrance and shielding of the phenolic hydroxyl group from the hydroxyl groups of the triethylene glycol molecule. The size of the xylenol molecule is also greater than that of m-cresol. As such, the number of xylenol molecules that can be accommodated by a given number of solvent molecules is smaller.

It is therefore to be expected that the recovery of the xylenol isomers should be lower than that of m-cresol, which should in turn be lower than that of phenol. Also, the sensitivity of xylenol recovery to changes in the various solvent ratios can be expected to be greater than that of the m-cresol recovery and phenol recovery.

Based on the recoveries of all the phenolic compounds under investigation, it is concluded that the hexane to feed and water to solvent ratios should be kept as low as possible and the solvent to feed ratio as high as possible. A solvent to feed ratio of 3.0 is preferable to one of 2.0 as an additional increase in phenolic recovery may be achieved. Also, the phenolic recovery is less sensitive to an increase in the hexane to feed and water to solvent ratios at a solvent to feed ratio of 3.0 than it is at one of 2.0. An increase in the solvent to feed ratio beyond 3.0 is not justified for any of the phenolic compounds.

As the effect of the hexane to feed ratio on phenolic recovery is greater at high water to solvent ratios and vice versa, a combination of high hexane to feed and high water to feed ratios should be avoided. As the recovery of the xylenol isomers is especially sensitive to an increase in the water to solvent ratio, water to solvent ratios greater than 0.3 should be avoided.

The decrease in phenolic recovery as the hexane to feed ratio is increased from 3.0 to 5.0 is small enough that the higher hexane to feed ratio would be justified, provided that it results in an increase in the separation efficiency of the solvent system.

5.4.2 Separation of Phenolic compounds from Aromatic Nitriles

5.4.2.1 General Trends in Phenol-Benzonitrile Separation

The separation factors for phenol-benzonitrile and the percentage of benzonitrile remaining in the solvent phase are listed in Table 5-2. The separation factors achieved for benzonitrile range from 4.0 to 18.1, i.e. a favourable separation of phenol from benzonitrile should be possible with the proposed solvent system.

The relationship between phenol recovery, benzonitrile recovery and the phenol-benzonitrile separation factor is illustrated in Figure 5.4-11.

It should be emphasised that, in order to obtain an effective separation between a phenolic compound and neutral oil or nitrogen base, the recovery of the neutral oil or nitrogen base should be as low as possible, while the recovery of the phenolic compound as well as the applicable separation factors should be as high as possible.

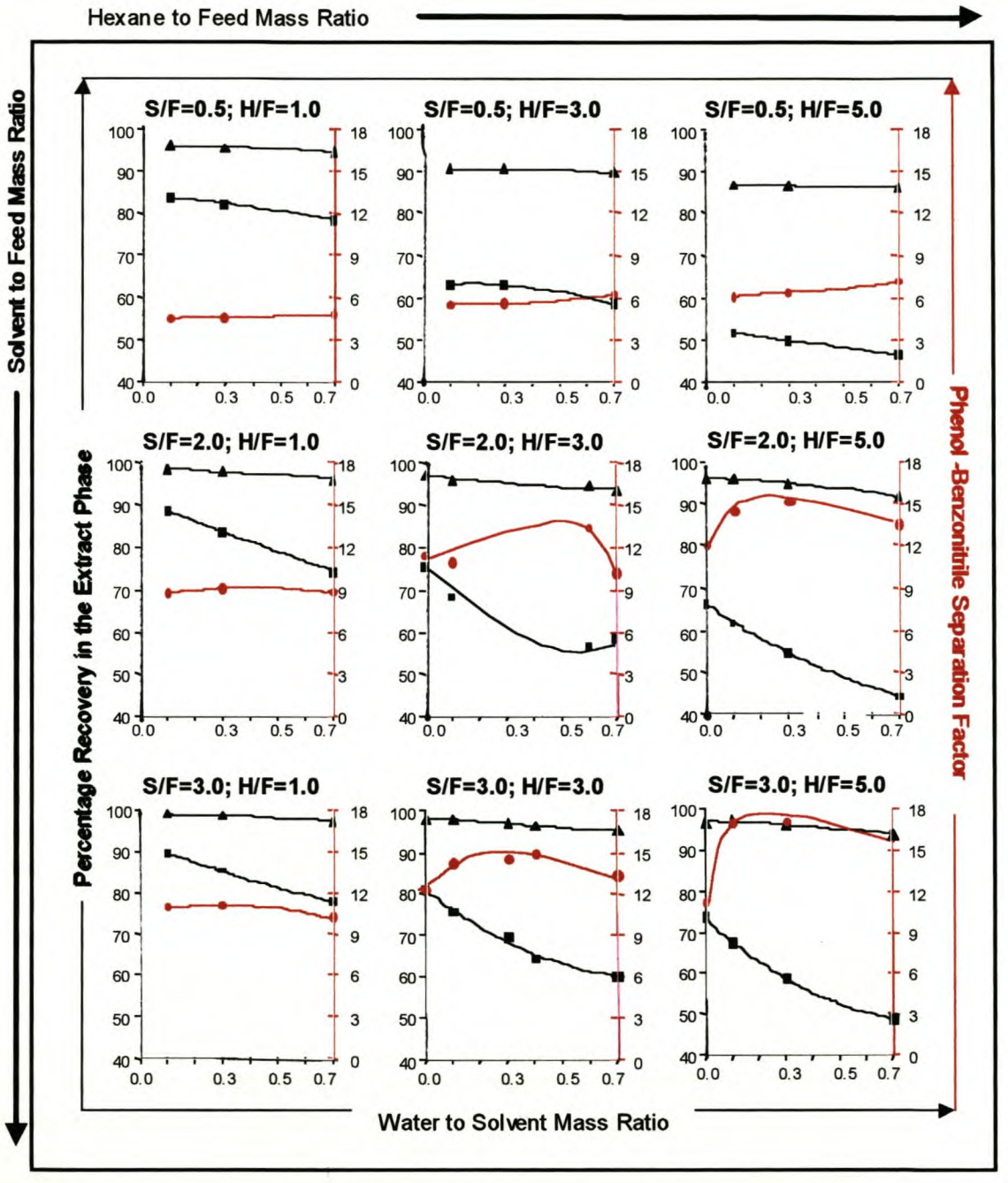


Figure 5.4-11. Effect of water to solvent ratio on phenol and benzonitrile recoveries and the phenol-benzonitrile separation factor at various solvent to feed and hexane to feed ratios.

▲ Phenol Recovery ■ Benzonitrile Recovery ●Phenol-Benzonitrile Separation Factor

A few general trends may be observed in Figure 5.4-11. Firstly, both the benzonitrile and phenol recovery decrease with an increase in the water to solvent ratio at all hexane to feed and water to solvent ratios. The decrease in benzonitrile recovery is however considerably greater, especially at a combination of high hexane to feed and solvent to feed ratios.

The recoveries of both benzonitrile and phenol are lower at higher hexane to feed ratios for corresponding water to solvent and solvent to feed ratios. Once again, the decrease in benzonitrile recovery is far more significant than the decrease in phenol recovery.

It can also be seen that, as with phenol, the recovery of benzonitrile is higher at higher solvent to feed ratios for corresponding water to solvent and hexane to feed ratios. The increase in benzonitrile with an increase in the solvent to feed ratio is however not significant at high hexane to feed ratios.

Like phenol, benzonitrile is readily soluble in both triethylene glycol and hexane. Unlike phenol, the solubility of benzonitrile in water is extremely low. Thus, an increase in the water to solvent ratio decreases the solubility of benzonitrile in the solvent phase. Also, benzonitrile is not held in the solvent phase by means of hydrogen bonds. The recovery of benzonitrile in the solvent phase will thus decrease far more than the recovery of phenol will with an increase in both the water to solvent and hexane to feed ratio.

As the benzonitrile molecules do not form hydrogen bonds with the solvent molecule, there is a far smaller incentive for the benzonitrile molecules to move from the hexane phase to the solvent phase than is the case with phenol. Therefore, an increase in the solvent to feed ratio at high hexane to feed ratios will have less of an effect on benzonitrile recovery than it would have on phenol recovery. Also, at high water to solvent ratios, the solubility of benzonitrile in the solvent phase is relatively low. A large increase in the solvent to feed ratio would thus be required to increase the recovery of the benzonitrile.

The effect of the various solvent ratios on the phenol-benzonitrile separation factor is less straightforward. At a low solvent to feed ratio of 0.5, an increase in the water to solvent ratio leads to a slight linear increase in the phenol - benzonitrile separation factor for all hexane to feed ratios. However, at solvent to feed ratios of 2.0 and 3.0, it is clear that an optimum water to solvent ratio exists. This optimum varies, depending on the hexane to feed and solvent to feed ratio. For example, for a constant solvent to feed ratio of 2.0 and hexane to feed ratio of 3.0, the optimum water to solvent ratio is approximately 0.6. At the same solvent to feed ratio, with a higher hexane ratio of 5.0, the optimum water to solvent ratio is much lower at approximately 0.15. The same shift in the optimum water to solvent ratio is observed if the hexane to feed ratio is increased from 3.0 to 5.0 at a solvent to feed ratio of 3.0.

Also, it the hexane to feed ratio is kept constant at 3.0 and the solvent to feed ratio is increased from 2.0 to 3.0, the optimum water to solvent ratio decreases from approximately 0.6 to 0.25. At a hexane to feed ratio of 5.0, an increase in the solvent to feed ratio does not lead to any noticeable change in the optimum water to solvent ratio.

It can therefore be concluded that the optimum water to solvent ratio decreases as the hexane to feed ratio increases; decreases as the solvent to feed ratio increases for a hexane to feed ratio of 3.0 and remains constant as the solvent to feed ratio increases at a hexane to feed ratio of 5.0.

To explain this trend, the effect of the phenol and benzonitrile recovery on the separation factor must be understood.

The separation factor and percentage recovery of a given component are defined in Equation 3.3-1 and 3.3-2 in Section 3.3 The relationship between the separation factor β_{AB} and the recovery R_A and R_B can be obtained by combining these equations:

$$\beta_{AB} = [R_A / (100- R_A)] / [R_B / (100- R_B] \quad (5.4\text{-}1)$$

where component A is the desired phenolic compound and component B is the neutral oil or nitrogen base.

Therefore, a decrease in the benzonitrile recovery, R_B, will lead to an increase in the separation factor while a decrease in the phenol recovery, R_A, will lead to a decrease in the separation factor. These effects counteract one another and, depending on which is more significant the separation factor will increase or decrease.

Another factor that must be taken into consideration is that if the recovery of one of the components is either very high or very low, a small change in the recovery of that component will have a large effect on the separation factor.

E.g. supposing the benzonitrile recovery remains constant and the phenol recovery increases with one percentage point from 98.0% to 99.0%. The separation factor will increase with a factor of 2.02. On the other hand, if the phenol recovery remains constant and the benzonitrile recovery decreases with 10 percentage points from 60.0% to 50.0 % the separation factor would only increase with a factor of 1.5. Thus, a relatively large decrease in the benzonitrile recovery may be required to counteract a small decrease in the phenol recovery.

It has been determined that at high hexane to feed ratios, the decrease in phenol recovery with an increase in water to solvent ratio is more significant than at low hexane to feed ratios. Thus, at high hexane to feed ratios, the decrease in phenol recovery with an increase in the water to solvent dominates the corresponding decrease in benzonitrile recovery and the separation factor decreases.

It can also be seen from Figure 5.4-11 that the benzonitrile separation factor becomes noticeably higher as the hexane to feed ratio increases from 1.0 to 3.0 to 5.0 for corresponding solvent to feed and water to solvent ratios. It has already been noted

that the decrease in phenol recovery is not significant as the hexane to feed ratio is increased from 3.0 to 5.0 at high solvent ratios. It can thus be concluded that a hexane to feed ratio of 5.0 should be used in conjunction with a solvent to feed ratio of 3.0 to achieve optimum phenol recovery and phenol-benzonitrile separation. A water to solvent of approximately 0.15 would be optimum under these conditions.

5.4.2.2 General Trends in m-Cresol – o-Tolunitrile Separation

The separation factors for m-cresol-o-tolunitrile and the percentage of o-tolunitrile remaining in the solvent phase are listed in Table 5-7. The m-cresol-o-tolunitrile separation factors are even better than the phenol-benzonitrile separation factors and range from 7.5 to 66.7.

The relationship between m-cresol recovery, o-tolunitrile recovery and m-cresol-o-tolunitrile separation factor is illustrated in Figure 5.4-12.

As can be expected, the same general trends may be observed for o-tolunitrile and m-cresol recoveries as for phenol and benzonitrile recoveries. Thus, the o-tolunitrile recovery decreases more significantly than the m-cresol recovery for an increase in water to solvent ratio. Both the o-tolunitrile and m-cresol recoveries decrease with an increase in the hexane to feed ratio and increase with an increase in the solvent to feed ratio. The effect of the various solvent ratios on o-tolunitrile are similar to those of benzonitrile as the solubility of o-tolunitrile and benzonitrile in triethylene glycol, water and hexane are similar.

As was the case with the phenol-benzonitrile separation factor, an optimum water to solvent ratio exists for the m-cresol-o-tolunitrile separation factor. This optimum is fairly constant at 0.1 for high solvent to feed ratios combined with high hexane to feed ratios.

The recovery of m-cresol was determined to be more sensitive to an increase in water to solvent ratio than that of phenol. The decrease in m-cresol recovery with an increase in water to solvent ratio will thus be more significant than the corresponding decrease in phenol recovery. It can therefore be expected that the decrease in m-cresol recovery will have a greater effect on the m-cresol - o-tolunitrile separation factor than that of phenol will have on the phenol-benzonitrile separation factor.

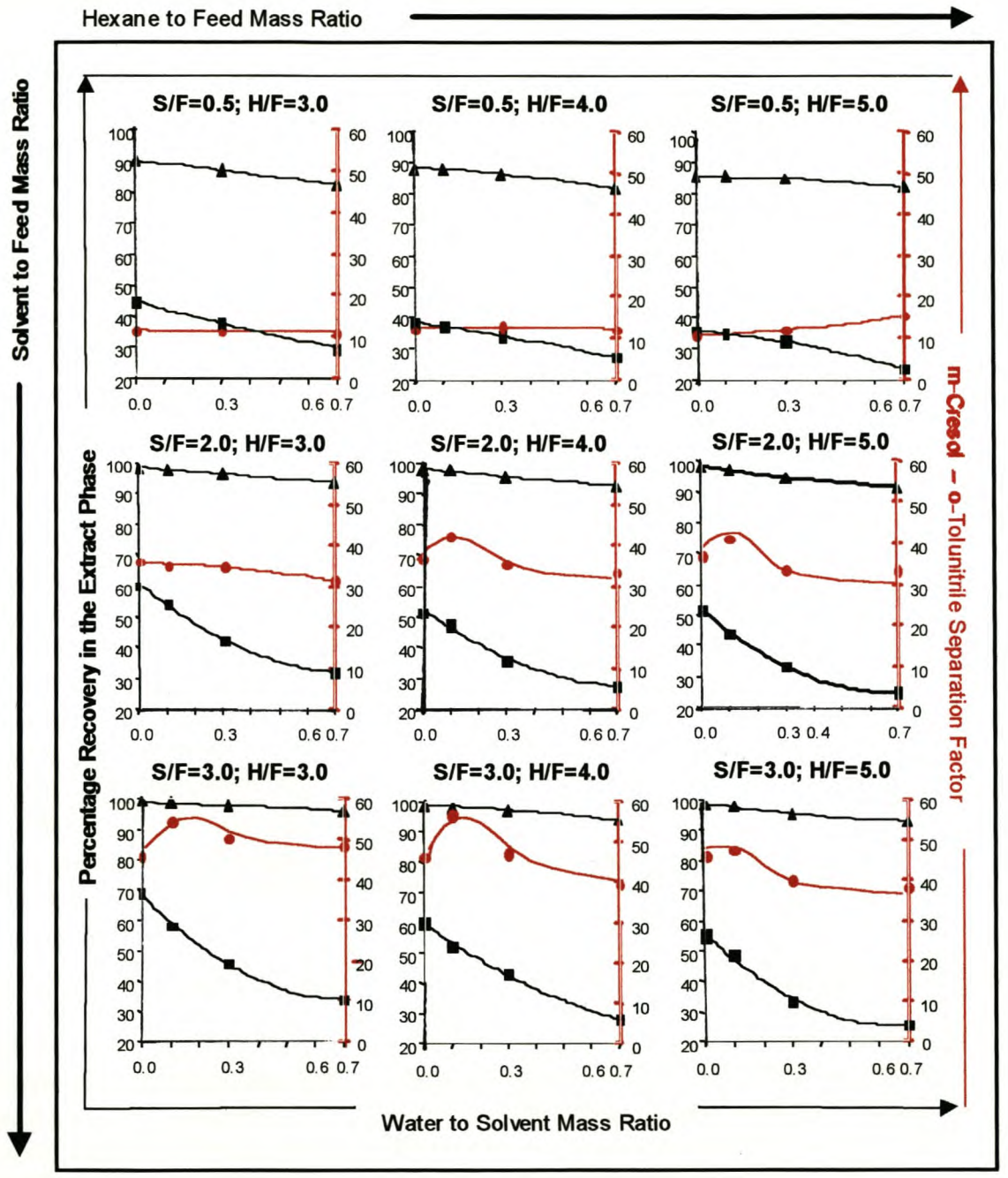


Figure 5.4-12. Effect of water to solvent ratio on m-cresol and o-tolunitrile recoveries and the m-cresol-o-tolunitrile separation factor at various solvent to feed and hexane to feed ratios.

▲ Phenol Recovery ■ Benzonitrile Recovery ● Phenol-Benzonitrile Separation Factor

5.4.2.3 Comparison of Phenol-Benzonitrile and m-Cresol-o-Tolunitrile Separation

It is apparent from Figure 5.4-11and Figure 5.4-12 that the separation factors achieved for m-cresol – o-tolunitrile are much larger than for phenol-benzonitrile, despite the fact that the recovery of phenol is better than that of m-cresol. This is due to the fact that the recovery of o-tolunitrile is considerably lower than that of benzonitrile. The recovery of benzonitrile ranges from 42.9 to 92.1% (see Table 5-2) while that of o-tolunitrile ranges from 19.8 to 85.9% (see Table 5-7). It can therefore be concluded that o-tolunitrile is more easily removed from the solvent phase than benzonitrile.

The effects of the solvent to feed, water to solvent and hexane to feed ratios on the m-cresol - o-tolunitrile and phenol – benzonitrile separation factors are illustrated for a wider range of solvent ratios in Figure 5.4-13, Figure 5.4-14 and Figure 5.4-15.

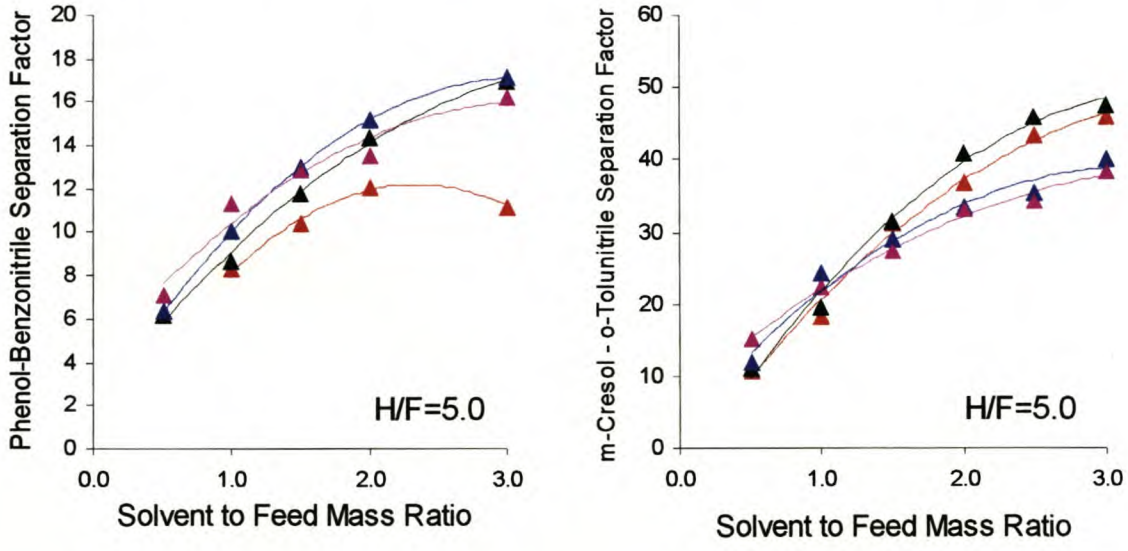


Figure 5.4-13. Effect of solvent to feed mass ratio on phenol-benzonitrile and m-cresol-o-tolunitrile separation factors at a constant hexane to feed mass ratio of 5.0. ▲ W/S=0.67 ▲ W/S=0.3 ▲ W/S=0.1 ▲ W/S=0.0

Figure 5.4-13 confirms that both the phenol – benzonitrile and the m-cresol - o-tolunitrile separation factors increase with an increase in the solvent to feed ratio for all water to solvent ratios. It is also clear that both separation factors increase significantly as the solvent to feed ratio is increased from 2.0 to 3.0. The use of the higher solvent to feed ratio is thus justified.

It was seen in Figure 5.4-11 and Figure 5.4-12 that the recovery of both the phenolic compounds and the aromatic nitriles increase with an increase in the solvent to feed ratio for all water to solvent and hexane to feed ratios. As the resulting effect is an increase in the corresponding separation factors, it can be concluded that the positive

effect of an increase in the phenolic compound recovery successfully counteracts the negative effect of an increase in the recovery of the aromatic nitriles.

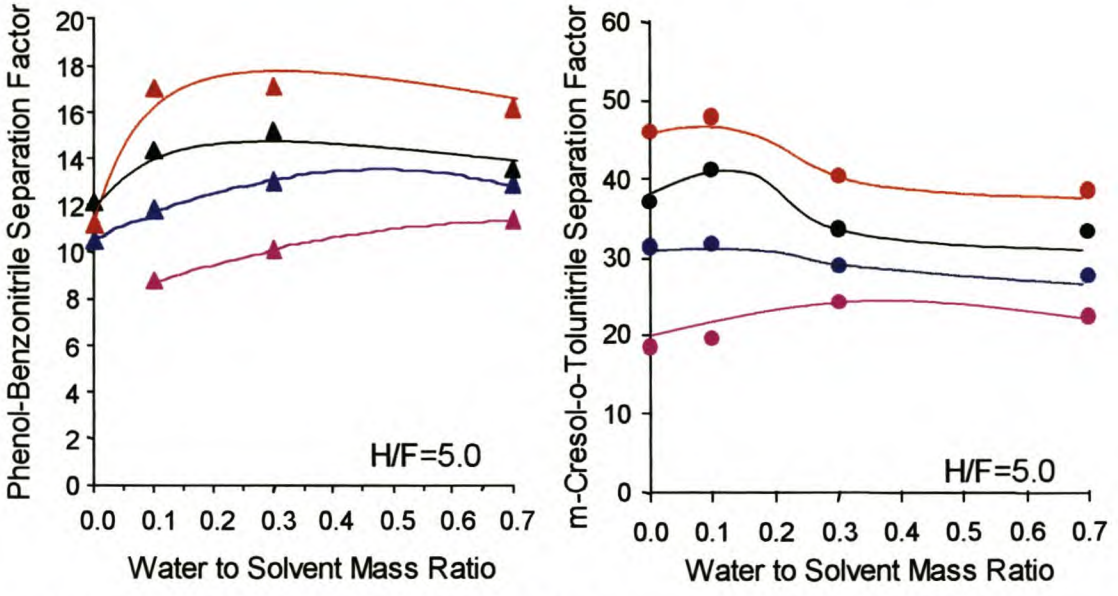


Figure 5.4-14. Effect of water to solvent mass ratio on phenol-benzonitrile and m-cresol-o-tolunitrile separation factors at a constant hexane to feed mass ratio of 5.0.

Phenol-Benzonitrile Separation Factor: ▲ S/F=1.0 ▲ S/F=1.5 ▲ S/F=2.0 ▲ S/F=3.0

m-Cresol-o-Tolunitrile Separation Factor: ● S/F=1.0 ● S/F=1.5 ● S/F=2.0 ● S/F=3.0

Figure 5.4-14 confirms the fact that the optimum water to solvent ratio for phenolic – aromatic nitrile separation at high hexane to feed ratios is approximately 0.1 for solvent to feed ratios in excess of 1.5. It is also once again apparent that an increase in the water to solvent ratio beyond a value of 0.1 has a larger negative effect on the m-cresol - o-tolunitrile separation factor than on the phenol – benzonitrile separation factor at corresponding solvent to feed ratios.

Figure 5.4-15 shows that the effect of the hexane to feed ratio on phenol – benzonitrile and m-cresol - o-tolunitrile separation factors differs. The phenol – benzonitrile separation factor increases in a linear manner as the hexane to feed ratio is increased from 0.5 to 5.0. The m-cresol - o-tolunitrile separation factor, however, initially increases as the hexane to feed ratio is increased and then decreases with a further increase in the hexane to feed ratio. This can be attributed to the conflicting influences of the decrease in o-tolunitrile and m-cresol recovery with an increase in the hexane to feed ratio. Initially the decrease in the o-tolunitrile is large enough and the decrease in m-cresol small enough to cause the separation factor to increase. At a certain point, the decrease in m-cresol recovery becomes too large for the decrease in o-tolunitrile to counteract it and the separation factor decreases. The optimum hexane to feed ratio is approximately 4.0 at a solvent ratio of 3.0 at various water to solvent ratios. As the phenol – benzonitrile separation is likely to be more difficult than the m-cresol - o-

tolunitrile separation, based on the relative values of the separation factors, the optimum hexane ratio for phenol – benzonitrile separation, i.e. 5.0 should be used.

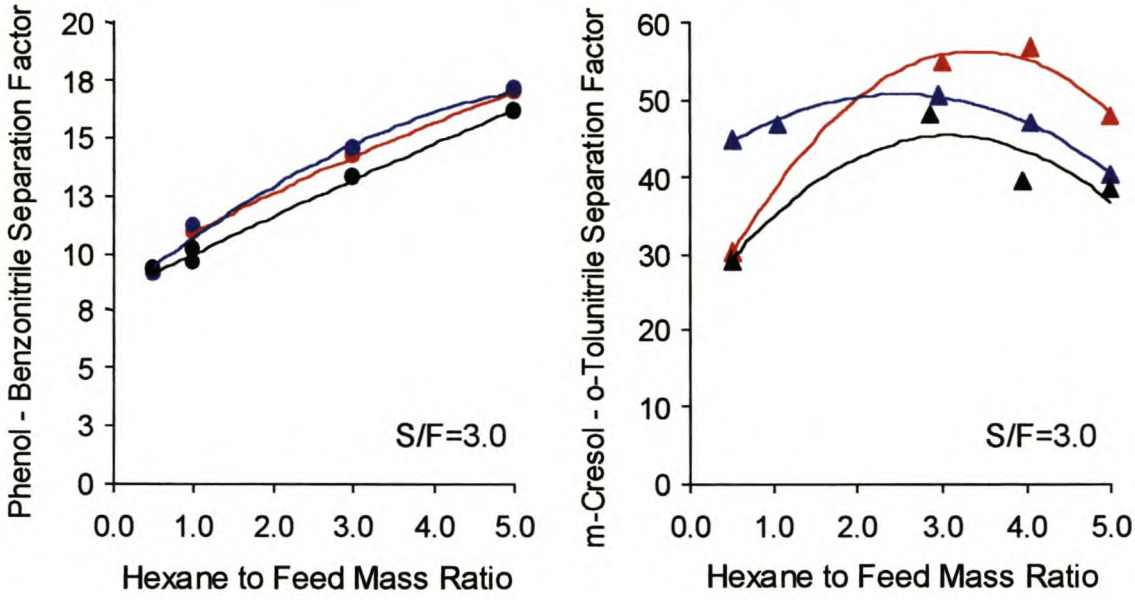


Figure 5.4-15. Effect of hexane to feed mass ratio on phenol-benzonitrile and m-cresol-o-tolunitrile separation factors at a constant solvent to feed mass ratio of 3.0.

Phenol-Benzonitrile Separation Factors: ● W/S=0.67 ● W/S=0.3 ● W/S=0.1
m-Cresol-o-Tolunitrile Separation Factors ▲ W/S=0.67 ▲ W/S=0.3 ▲ W/S=0.1

It can thus be concluded that a combination of a solvent to feed ratio of 3.0, a water to solvent ratio of 0.1 and a hexane to feed ratio of 5.0 will be optimum for the separation of phenolic compounds from aromatic nitriles.

5.4.3 Separation of Phenolic compounds from Aromatic Amines

5.4.3.1 General Trends in Phenol - Aniline Separation

The phenol - aniline separation factors range from 1.6 - 3.7 (see Table 5-2). As such, the separation of phenol from aniline, while more difficult than that of phenol from benzonitrile, should be feasible. It can further be concluded from a comparison of the separation factors obtained for phenol relative to benzonitrile, aniline, 5-et-2-me-pyridine and mesitylene that the separation of phenol from aniline is the most difficult separation to effect in the phenol system.

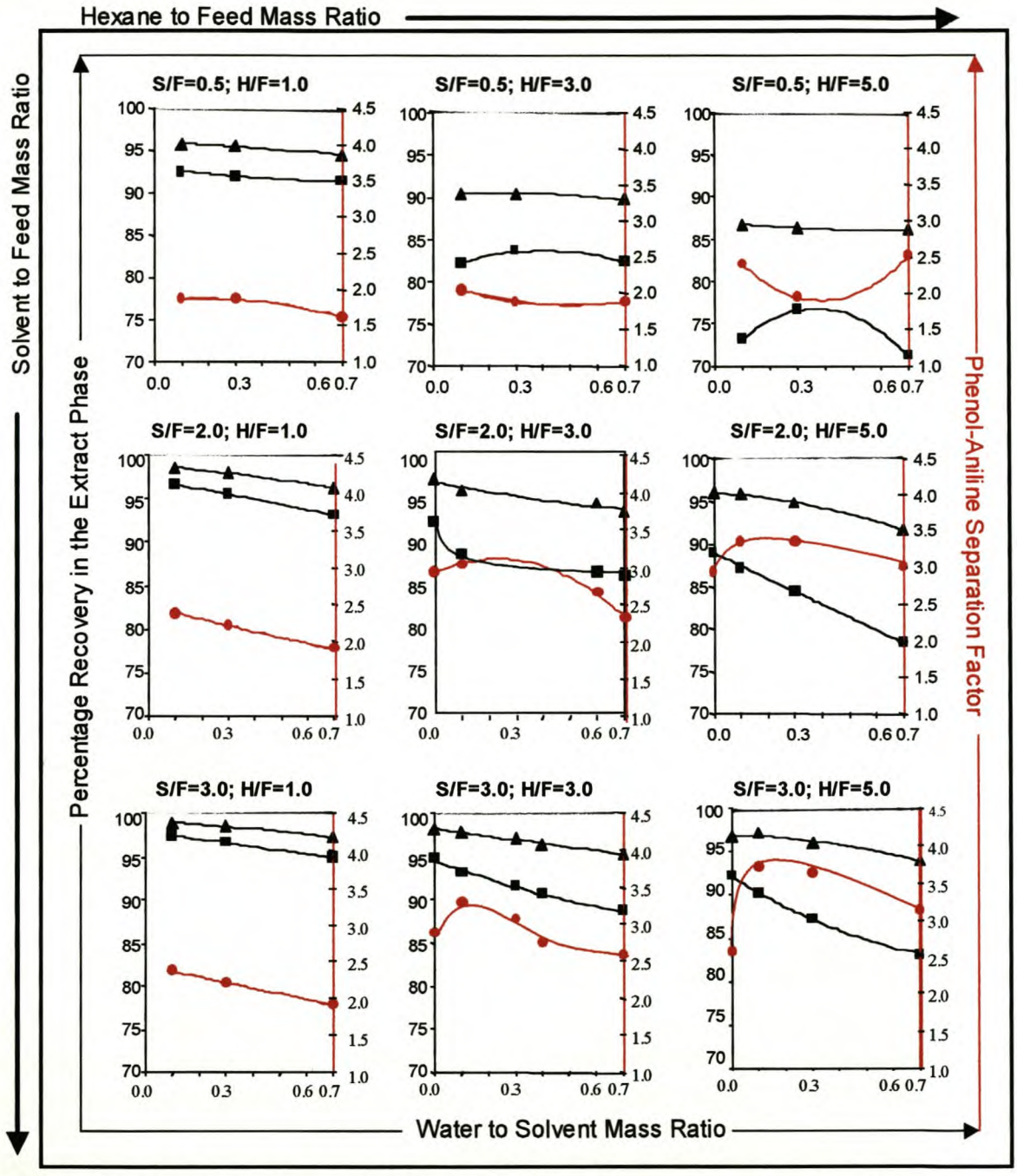


Figure 5.4-16. Effect of water to solvent ratio on phenol and aniline recoveries and the phenol-aniline separation factor at various solvent to feed and hexane to feed ratios.

▲ Phenol Recovery ■ Aniline Recovery ● Phenol-Aniline Separation Factor

The recovery of aniline in the solvent phase is fairly high and ranges from 71.1 to 98.2%. The recovery of aniline is however significantly lower than that of phenol which ranges from 86.1 to 99.1% over the same series of batch extractions.

The reason for the high aniline recovery is that the amine group is also capable of forming hydrogen bonds with the triethylene glycol molecules, i.e. the affinity of aniline

for the solvent phase is high. As was previously noted, the hydrogen bond formed between hydrogen and nitrogen is weaker than that formed between hydrogen and oxygen. Thus the hydrogen bonds formed between aniline and triethylene glycol are weaker than those formed between phenol and triethylene glycol. This results in the observed fact that the phenol recovery is higher than the aniline recovery. The aniline recovery should also be more sensitive to the negative effects of an increase in the water to solvent and hexane to feed ratios.

It is apparent from Figure 5.4-16, that this is indeed the case. At solvent to feed ratios of 2.0 and 3.0 combined with hexane to feed ratios of 3.0 and 5.0, the decrease in aniline recovery with an increase in the water to solvent ratio is noticeably greater than that of phenol. E.g. at a hexane to feed ratio of 5.0 and solvent to feed ratio of 2.0, an increase in the water to solvent ratio from 0.0 to 0.67 results in a decrease in aniline recovery of 10.7 percentage points (89.0% to 78.3%). The corresponding decrease in phenol recovery is less than half the amount: 4.4 percentage points (96.0% to 91.6%). The difference is even more pronounced at the same hexane to feed ratio with a higher solvent to feed ratio of 3.0. The aniline recovery decreases with 9.0 percentage points from 92.2 to 83.2 % while the phenol recovery decreases by only 2.9 percentage points from 96.8 to 93.9%.

It is interesting to note that, as has been observed for phenol recovery, the effect of the water to solvent ratio on the decrease in aniline recovery is less severe at a solvent to feed ratio of 3.0 than at one of 2.0. The similarity between aniline and phenol recovery in this respect can be attributed to the fact that both have a similar affinity for the solvent phase. It is also worth noting that the effect of the water to solvent ratio on the aniline recovery is not reduced as much as is the effect of the water to solvent ratio on the phenol recovery as the solvent to feed ratio is increased. Thus, at a constant hexane to feed ratio, the percentage point decrease in phenol recovery (over a water to solvent ratio of 0.0 to 0.7) is reduced by 35% from 4.4 to 2.9 as the solvent to feed ratio increases from 2.0 to 3.0. The corresponding percentage point decrease in aniline recovery is reduced by only 15% from 10.7 to 9.0.

The slightly lower affinity of aniline for the solvent phase may thus be exploited through manipulation of the various solvent ratios to effect a separation from phenol.

From Figure 5.4-16 it can further be seen that the optimum water to solvent ratio is 0.1 for a combination of the high solvent to feed and hexane to feed ratios. The separation factors noticeably increase with an increase in both the solvent to feed and hexane to feed ratios.

5.4.3.2 General Trends in m-Cresol – o-Toluidine Separation

The m-cresol - o-toluidine separation factors are significantly higher than the corresponding phenol - aniline separation factors and range from 3.9 to 16.3 (see Table 5-7). This can be attributed to the fact that the recovery of o-toluidine in the solvent phase is much lower than that of aniline. The recoveries achieved for aniline range from 71.1 to 98.2% while those of o-toluidine range from 43.2 to 96.0%. The corresponding m-cresol recoveries range from 81.8 to 99.5%.

Therefore, while o-toluidine is also capable of forming hydrogen bonds with the triethylene glycol molecules in the solvent phase, it is clearly less prone to doing so than aniline is. This is due to the fact that the o-toluidine molecule contains a methyl group, which is situated on a carbon atom adjacent to the amine group on the aromatic ring. This methyl group shields the amine group from the hydroxyl groups of the triethylene glycol molecule. The potential for o-toluidine to form hydrogen bonds is thus lower than that of aniline. The recovery of o-toluidine is consequently lower.

The relationship between m-cresol recovery, o-toluidine recovery and m-cresol - o-toluidine separation factors is illustrated in Figure 5.4-17.

As with phenol and aniline, the recovery of both m-cresol and o-toluidine decrease with and increase in the water to solvent ratio. Also, just as the decrease in aniline recovery is more significant than the decrease in phenol recovery, so the decrease in o-toluidine recovery is more significant the decrease in m-cresol recovery.

The substantially lower recovery of o-toluidine in comparison to that of m-cresol is due to the fact that the hydrogen bonds formed by m-cresol are considerably stronger than those of o-toluidine. As the incentive to form hydrogen bonds is stronger for m-cresol, the shielding effect of the m-cresol methyl group can be expected to have less of an effect than the methyl group of o-toluidine has. Also, in the m-cresol molecule, the methyl group is further removed from the hydroxyl group than the methyl group of the o-toluidine molecule is removed from the amine group. It will therefore shield the phenolic hydroxyl group less than the methyl group of the o-toluidine molecule will shield the amine group.

Therefore, o-toluidine will be more sensitive to changes in water to solvent and hexane to feed ratios than m-cresol.

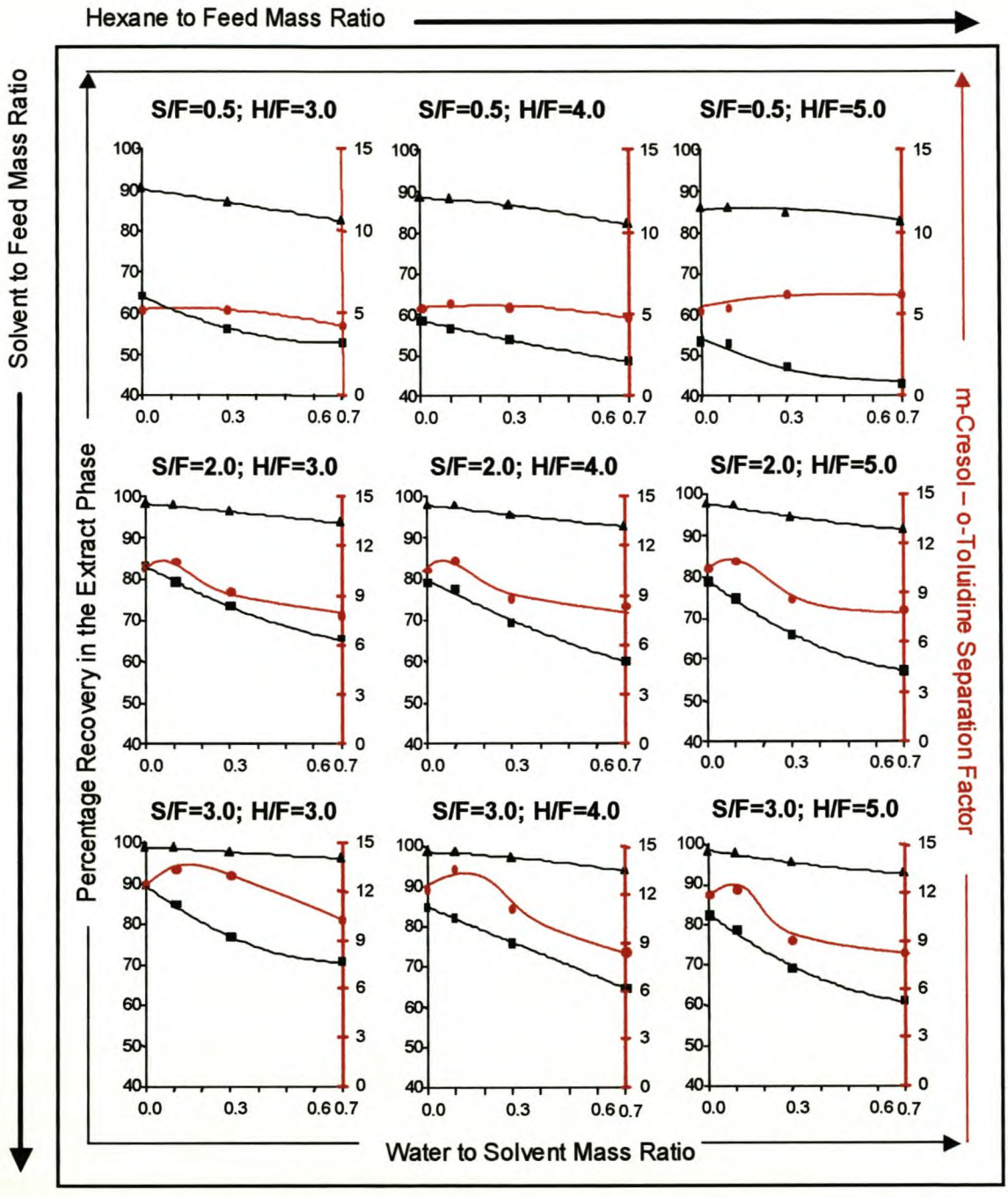


Figure 5.4-17. Effect of water to solvent ratio on m-cresol and o-toluidine recoveries and the m-cresol - o-toluidine separation factor at various solvent to feed and hexane to feed ratios.

▲ m-Cresol Recovery ■ o-Toluidine Recovery ● m-Cresol-o-Toluidine Separation Factor

As was the case with the phenol - aniline separation factor, the m-cresol - o-toluidine separation factor is highest at water to solvent ratios of 0.1 for high solvent to feed and hexane to feed ratios. The effect of solvent to feed and hexane to feed is illustrated in more clearly in the following section.

5.4.3.3 Comparison of Phenol - Aniline and m-Cresol - o-Toluidine Separation

The effect of the solvent to feed ratio on phenol - aniline and m-cresol - o-toluidine separation factors is illustrated in Figure 5.4-18.

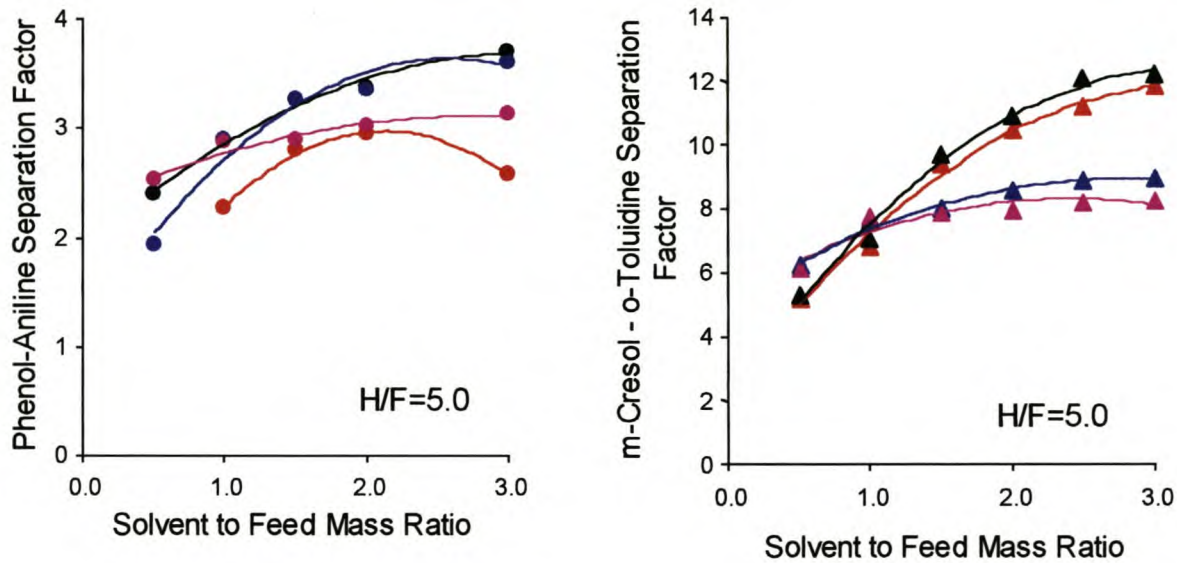


Figure 5.4-18. Effect of solvent to feed mass ratio on phenol-aniline and m-cresol-o-toluidine separation factors at a constant hexane to feed mass ratio of 5.0.

Phenol - Aniline Separation Factor: ● **W/S=0.67** ● **W/S=0.3** ● **W/S=0.1** ● **W/S=0.0**

m-Cresol-o-Toluidine Separation Factor: ▲ **W/S=0.67** ▲ **W/S=0.3** ▲ **W/S=0.1** ▲ **W/S=0.0**

From Figure 5.4-18 it can be seen that, at constant hexane to feed and water to solvent ratios, an increase in solvent to feed ratio leads to an increase in both the phenol - aniline and m-cresol - o-toluidine separation factors. The single exception is that of the phenol - aniline separation factor at a water to solvent of 0.0. It can further be inferred from Figure 5.4-18 that an increase in solvent to feed ratio beyond a value of 3.0 will not result in an increase in the phenolic-aromatic amine separation factors.

The effect of the water to solvent ratio on the m-cresol - o-toluidine is also clearly illustrated in Figure 5.4-18. Not only are the m-cresol - o-toluidine separation factors lower at water to solvent ratios of 0.3 and 0.67, the effect of an increase in the solvent to feed ratio on the separation factors at these high water to solvent ratios is noticeably lower than at water to solvent ratios of 0.0 and 0.1.

This effect of the water to solvent ratio is further illustrated in Figure 5.4-19.

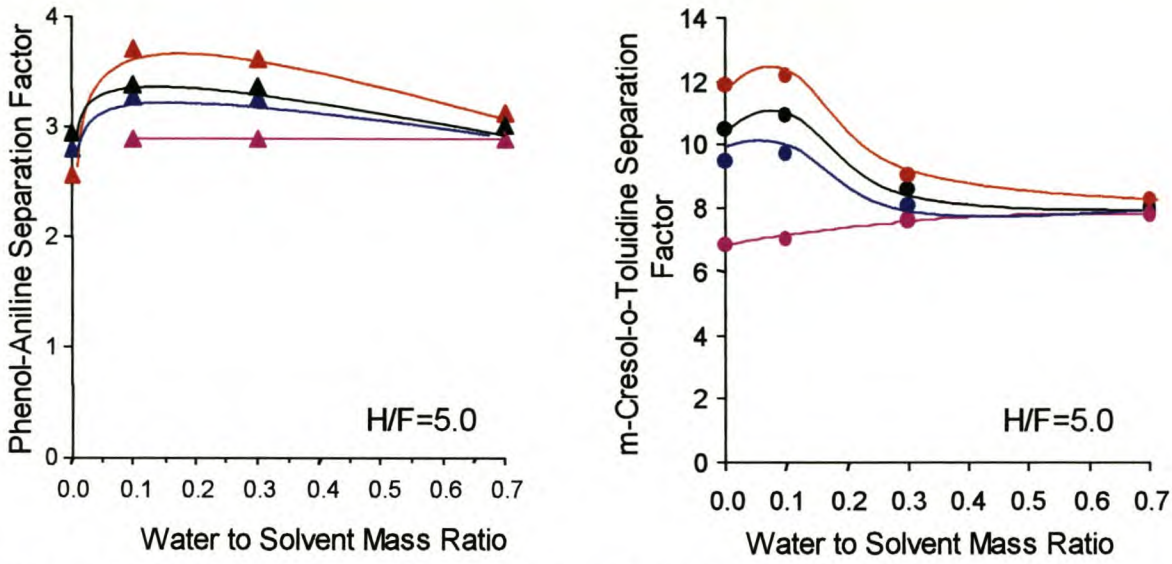


Figure 5.4-19. Effect of water to solvent mass ratio on phenol - aniline and m-cresol - o-toluidine separation factors at a constant hexane to feed mass ratio of 5.0.

Phenol-Aniline Separation Factor ▲ S/F=1.0 ▲ S/F=1.5 ▲ S/F=2.0 ▲ S/F=3.0
m-Cresol-o-Toluidine Separation Factor: ● S/F=1.0 ● S/F=1.5 ● S/F=2.0 ● S/F=3.0

In Figure 5.4-19, it is confirmed that at a high hexane to feed ratio of 5.0 the optimum water to solvent ratio is approximately 0.1 for all solvent to feed ratios. It is interesting to note that a small increase in the water to solvent ratio beyond a value of 0.1 leads to a significant decrease in the m-cresol - o-toluidine separation factor. This sharp decrease in the separation factor is however misleading. At a hexane to feed ratio of 5.0 and a solvent to feed ratio of 3.0, the o-toluidine recovery decreases from 78.6% to 69.3% as the water to solvent ratio is increased from 0.1 to 0.3. The corresponding decrease in m-cresol is much smaller: from 97.8% to 95.3%. The small decrease in m-cresol recovery causes the separation factor to decrease by approximately 25% from 12.2 to 9.0.

Therefore, while the optimum water to solvent ratio for the separation of phenolic compounds from the aromatic amines is clearly 0.1, a higher water to solvent ratio may be justified for the removal of larger amounts of the aromatic amines from the extract phase as the corresponding decrease in phenolic recovery is not significant.

The effect of the hexane to feed ratio is illustrated in Figure 5.4-20.

Figure 5.4-20 confirms that, at a solvent to feed ratio of 3.0, an increase in the hexane to feed ratio results in an increase in the phenol - aniline separation factor at all water to solvent ratios. While the effect of the increased hexane to feed ratio is the same at all solvent to feed ratios, it is once again clear that, at corresponding hexane and solvent to feed ratios, the phenol - aniline separation factor is lower as the water to solvent ratio is increased

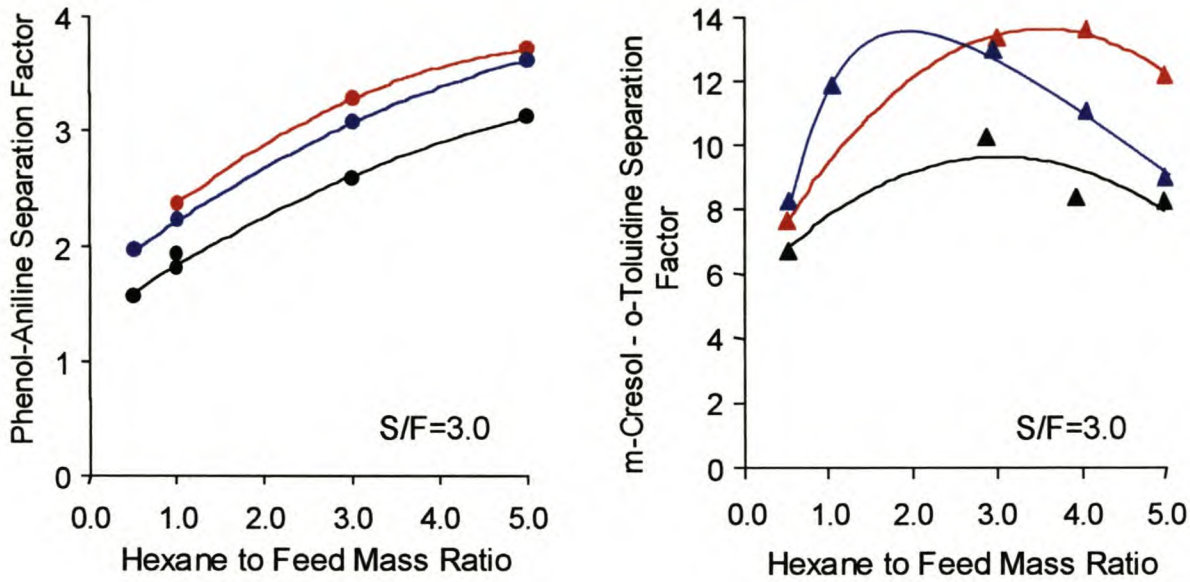


Figure 5.4-20. Effect of hexane to feed mass ratio on phenol-aniline and m-cresol-o-toluidine separation factors at a constant solvent to feed mass ratio of 3.0.
Phenol-Aniline Separation Factors: ● W/S=0.67 ● W/S=0.3 ● W/S=0.1
m-Cresol-o-Toluidine Separation Factors ▲ W/S=0.67 ▲ W/S=0.3 ▲ W/S=0.1

As was the case for the m-cresol - o-tolunitrile separation factors, an optimum hexane to feed ratio exists for the m-cresol - o-toluidine separation factor. This decrease in the m-cresol - o-toluidine separation factor can also be attributed to the overwhelming effect that a decrease in m-cresol recovery has on the separation factor. At a solvent to feed ratio of 3.0 and water to solvent ratio of 0.1, the optimum m-cresol - o-toluidine separation factor is achieved at a hexane to feed ratio of 3.0. The o-toluidine recovery at this point is 84.9% and that of m-cresol is 98.7%. If the hexane to feed ratio is increased to 5.0 at the same solvent to feed and water to solvent ratios, the o-toluidine recovery decreases by 6.3 percentage points to 78.6% while the m-cresol recovery decreases with only 0.9 percentage points to 97.8%. Thus, the decrease in the m-cresol - o-toluidine separation factor is misleading. Therefore, the decrease in both the m-cresol and o-toluidine recoveries should be taken into consideration when investigating the optimum hexane to feed ratio.

As the phenol - aniline separation factors are significantly lower than the m-cresol - o-toluidine separation factors, it can be concluded that the removal of aniline from the extract phase will be more difficult than the removal of o-toluidine. The optimum solvent ratios for aniline should thus be given preference. Therefore, in the case of phenolic - aromatic amine separation, the optimum solvent to feed ratio is 3.0; the optimum water to solvent ratio is 0.1 and the optimum hexane to feed ratio is 5.0. A

larger water to solvent ratio may be used to ensure a greater removal of the aromatic amines from the solvent phase.

5.4.4 Separation of Phenol from 5-Et-2-me-pyridine

The phenol - 5-et-2-me-pyridine separation factors obtained are very good and range from 6.4 to 41.7 (see Table 5-2).

The nitrogen of a pyridine molecule has a nonbonding electron pair that lies in the plane of the molecule away from the aromatic ring. Therefore, because it has a nonbonding electron pair that is not involved in the aromatic sextet, pyridine acts in a manner analogous to that of an amine [84]. I.e. pyridine is capable of forming hydrogen bonds. It is also miscible with water. However, as the alkyl substitution of the pyridine ring increases, the ability of pyridine to form hydrogen bonds, as well as its water solubility decreases dramatically. The higher alkyl substituted pyridines, such as 5-et-2-me-pyridine, are only sparingly soluble in water.

The much weaker potential of 5-et-2-me-pyridine to form hydrogen bonds is reflected in the fact that the phenol - 5-et-2-me-pyridine separation factors are considerably higher than the corresponding phenol - aniline separation factors.

The relationship between the 5-et-2-me-pyridine recovery, phenol recovery and phenol - 5-et-2-me-pyridine separation factor is illustrated in Figure 5.4-21.

The same general trends are observed for 5-et-2-me-pyridine recovery as for the recovery of the aromatic amines and nitriles. I.e. the 5-et-2-me-pyridine recovery decreases with an increase in both the water to solvent and hexane to feed ratios and increases with an increase in the solvent to feed ratio. This is to be expected as 5-et-2-me-pyridine is readily soluble in both hexane and triethylene glycol and only sparingly soluble in water. The 5-et-2-me-pyridine recovery should thus be subject to the same conflicting driving forces as regards dissolving in triethylene glycol and hexane as the aniline and benzonitrile recoveries.

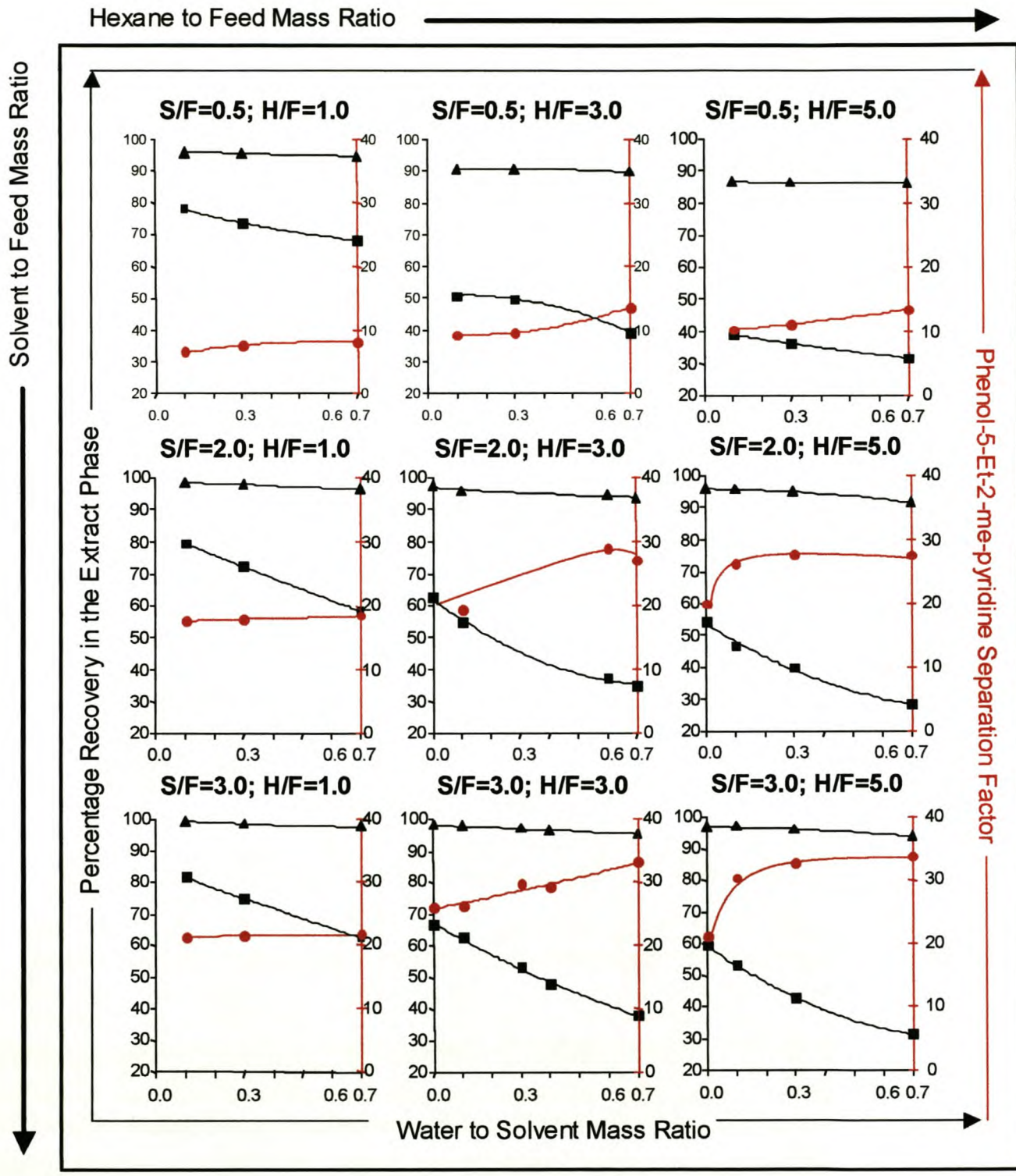


Figure 5.4-21. Effect of water to solvent ratio on m-cresol and o-toluidine recoveries and the m-cresol - o-toluidine separation factor at various solvent to feed and hexane to feed ratios.

▲ m-Cresol Recovery ■ o-Toluidine Recovery ● m-Cresol-o-Toluidine Separation Factor

The effect of the solvent to feed, hexane to feed and water to solvent ratios on phenol - 5-et-2-me-pyridine separation factors is illustrated in more detail in Figure 5.4-22, Figure 5.4-23 and Figure 5.4-24.

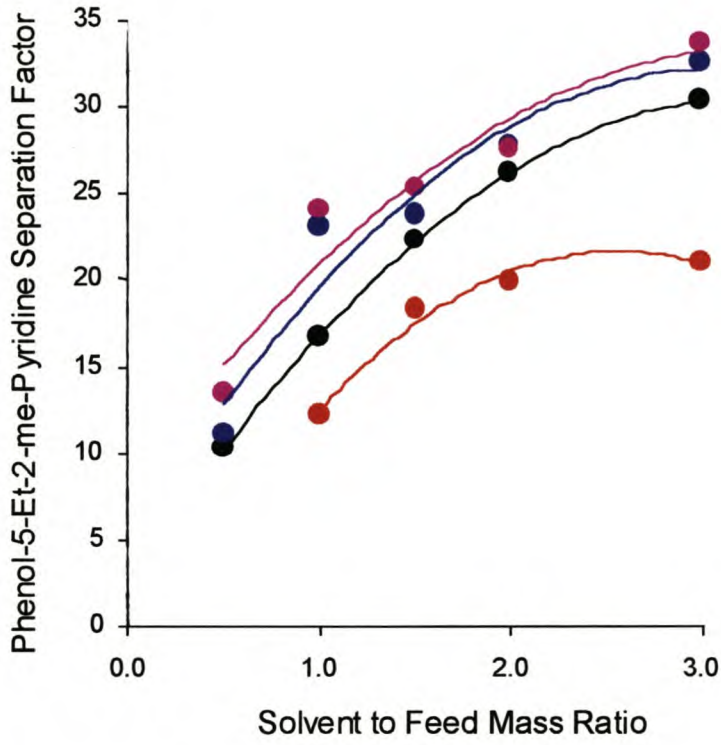


Figure 5.4-22. Effect of solvent to feed mass ratio on the phenol - 5-et-2-me-pyridine separation factor at a constant hexane to feed mass ratio of 5.0.

W/S=0.67 W/S=0.3 W/S=0.1 W/S=0.0

From Figure 5.4-22 it can be seen that, at a high hexane to feed ratio of 5.0, the phenol - 5-et-2-me-pyridine separation factor increases with and increase in the solvent to feed ratio for all water to solvent ratios. Therefore, as was the case for the phenol-aniline and phenol-benzonitrile it can be concluded that the increase in phenol recovery dominates the effect on the separation factor.

From Figure 5.4-23 it can be seen that, at a high hexane to feed ratio of 5.0, and solvent to feed ratios in excess of 1.0, the phenol - 5-et-2-me-pyridine separation factor initially increases as the water to solvent ratio is increased from 0.0 to 0.1. A further increase in the water to solvent ratio does not result in any noticeable increase in the phenol - 5-et-2-me-pyridine separation factor. It is however interesting to note that the phenol - 5-et-2-me-pyridine separation factor does not decrease with an increase in the water to solvent ratio beyond the value of 0.1 as the phenol - aniline and phenol - benzonitrile separation factors did. The phenol - 5-et-2-me-pyridine, phenol - aniline and phenol-benzonitrile separation factors were determined simultaneously. The decrease in phenol recovery is therefore identical for all three cases. The effect of the water to solvent ratio on the recoveries of benzonitrile, aniline and 5-et-2-me-pyridine must

therefore differ. As the phenol - 5-et-2-me-pyridine separation factor does not decrease with an increase in water to solvent ratio, it can be concluded that, for a hexane to feed ratio of 5.0, the decrease in 5-et-2-me-pyridine recovery is larger than the decrease in either the aniline or benzonitrile recoveries at all solvent to feed ratios and water to solvent ratios. Figure 5.4-21 shows that the phenol - 5-et-2-me-pyridine separation factor also does not decrease at lower hexane to feed ratios. Therefore, it can be concluded that the removal of 5-et-2-me-pyridine from the solvent phase is simpler than the removal of benzonitrile or aniline at all solvent ratios.

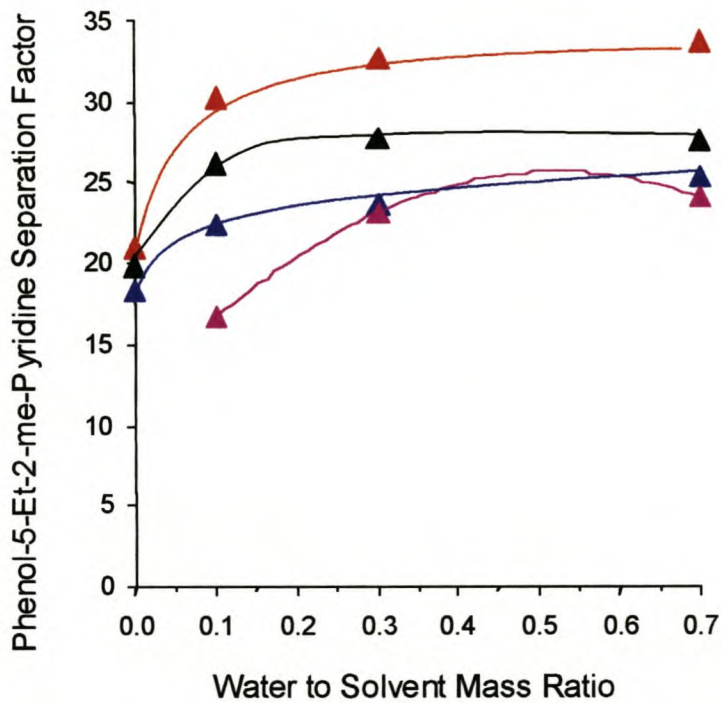


Figure 5.4-23. Effect of water to solvent mass ratio on phenol - 5-et-2-me-pyridine separation factors at a constant hexane to feed mass ratio of 5.0.

▲ S/F=1.0 ▲ S/F=1.5▲ S/F=2.0▲ S/F=3.0

The effect of the hexane to feed ratio on the phenol - 5-et-2-me-pyridine separation factor is shown in Figure 5.4-24. As is expected, at a constant solvent to feed ratio of 3.0, an increase in the hexane to feed ratio leads to an increase in the phenol - 5-et-2-me-pyridine at all water to solvent ratios.

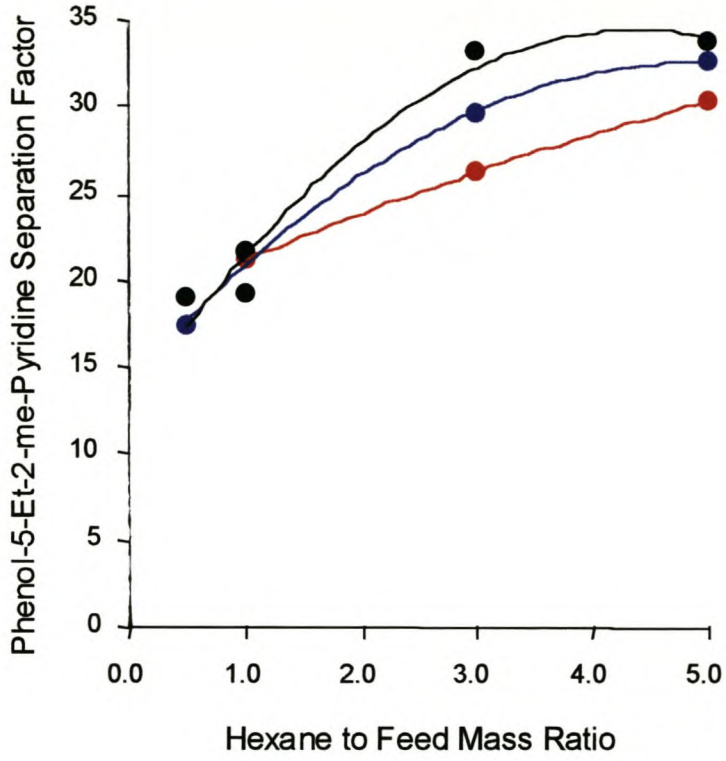


Figure 5.4-24. Effect of hexane to feed mass ratio on phenol-5-et-2-me-pyridine separation factors at a constant solvent to feed mass ratio of 3.0.

● **W/S=0.67** ● **W/S=0.3** ● **W/S=0.1**

The optimum hexane to feed and solvent to feed for the separation of 5-et-2-me-pyridine and phenol is therefore 5.0 and 3.0 respectively. These ratios correspond with those determined for the separation of phenol and m-cresol from the aromatic amines and nitriles. Based on separation factors, the optimum water to solvent ratio is approximately 0.1 for the separation of phenolic compounds from all the nitrogen bases investigate. The use of a higher water to solvent ratio is however justified on the grounds that the recoveries of aniline, benzonitrile and 5-et-2-me-pyridine all decrease with a further increase in the water to solvent ratio.

5.4.5 Separation of Phenolic Compounds from Paraffins

The m-Cresol – undecane and xylenol – dodecane separation factors obtained with the proposed solvent system are extremely high (see Table 5-7 and Table 5-10 respectively). m-Cresol – undecane separation factors range from 87.2 to values in excess of 46 000. Xylenol – dodecane separation factors range from 204.3 to values in excess of 63 000. The recoveries of undecane and dodecane are extremely low. On average 1.1% of the feed undecane remains in the solvent phase, with recoveries greater than 4.0% almost exclusively occurring at hexane to feed ratios of 0.5. Dodecane recoveries are even lower, on average 0.3%. The highest dodecane recovery obtained is only 1.5%.

The triviality of the separation of phenolic compounds from paraffins with the proposed solvent is ensured by the fact that undecane and dodecane are both immiscible with both triethylene glycol and water. As undecane and dodecane are homologues of hexane, they should fulfil the same antisolvent function as hexane. Thus, the presence of undecane and dodecane in the feed should enhance the separation of the phenolic compounds from the nitrogen bases, nitriles and amines.

5.4.6 Separation of Xylenol from Naphthalene

It can be seen from Table 5-10 that the separation of the xylenol isomers from naphthalene is simple using the proposed solvent system. Very high xylenol – naphthalene separation factors, ranging from 36.3 to 170.3 are obtained. The percentage of feed naphthalene remaining in the solvent phase ranges from 1.6% to 47.0%. The average percentage recovery of naphthalene in the solvent phase is 9.7%. I.e. on average 90.3% of the naphthalene in the feed is removed in a single extraction step.

The effect of the solvent to feed ratio on naphthalene recovery and xylenol - naphthalene separation factors is shown in Figure 5.4-25.

At a constant hexane to feed ratio of 5.0, an increase in solvent to feed ratio leads to an increase in the naphthalene recovery for all water to solvent ratios. This is to be expected as naphthalene has a limited solubility in triethylene glycol. This solubility is however significantly decreased as the water content of the solvent phase is increased. Thus the increase in the percentage of feed naphthalene remaining in the solvent phase with an increase in the solvent to feed ratio is more significant at the low water to solvent ratio of 0.1 than it is at higher water to solvent ratios of 0.3 and 0.67.

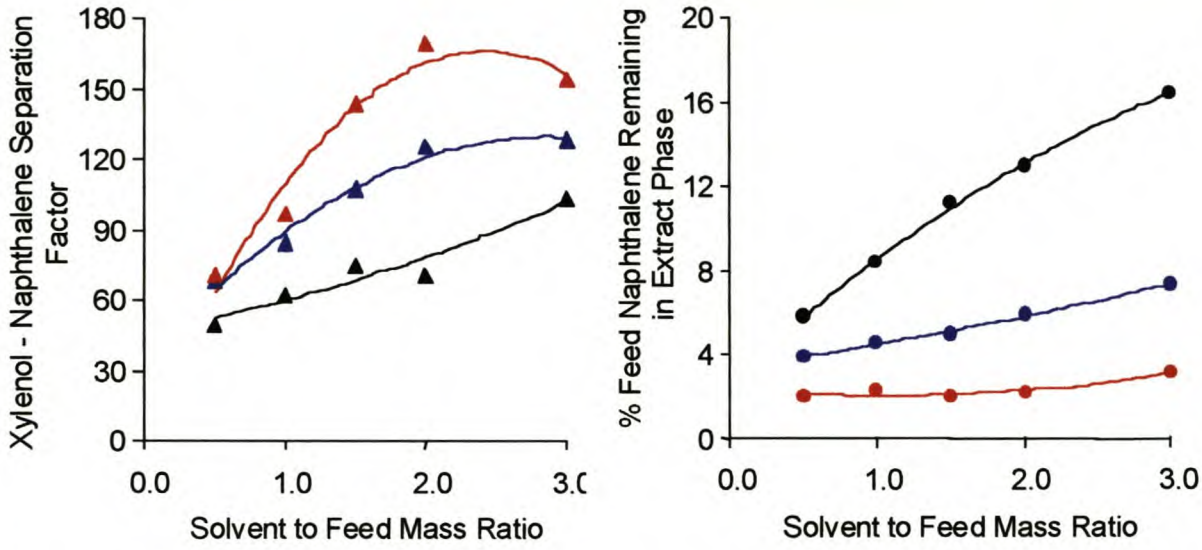


Figure 5.4-25. Effect of solvent to feed mass ratio on the xylenol - naphthalene separation factor and percentage of feed naphthalene remaining in the extract phase. Hexane to feed mass ratio = 5.0.

Xylenol - naphthalene separation factor : ▲W/S=0.67 ▲ W/S=0.3 ▲ W/S=0.1

Naphthalene recovery : ●W/S=0.67 ● W/S=0.3 ● W/S=0.1

The xylenol - naphthalene separation factor increases with an increase in the solvent to feed ratio from 0.5 to 2.0, despite the increase in naphthalene recovery. it can thus be concluded that the positive effect the corresponding increase in xylenol recovery on the separation factor successfully counteracts the negative effect of the increase in naphthalene recovery.

However, while a further increase in the solvent to feed ratio results in an increase in the xylenol - naphthalene separation factor at water to solvent ratios of 0.1 and 0.3, at the high water to solvent ratio of 0.67, the opposite occurs. In Figure 5.4-7 it is shown that an increase in the solvent to feed ratio from 2.0 to 3.0 has a very small effect on the recovery of all three xylenol isomers, especially at high water to solvent ratios. Thus, at a water to solvent ratio of 0.67, a very small increase in napthalene recovery will be sufficient to cause a decrease in the xylenol - naphthalene separation factor.

The effect of the water to solvent ratio is illustrated in Figure 5.4-26. An increase in the water to solvent ratio results in a decrease in the percentage of feed naphthalene remaining in the solvent phase and consequently results in an increase in the xylenol - naphthalene separation factor.

It is also clear from Figure 5.4-26 that the biggest decrease in naphthalene recovery occurs as the water to solvent ratio is increased from 0.1 to 0.3. A further increase in the water to solvent has a negligible effect on naphthalene recovery. Therefore, in

terms of removal of naphthalene from the solvent phase a high water to solvent ratio is not justified.

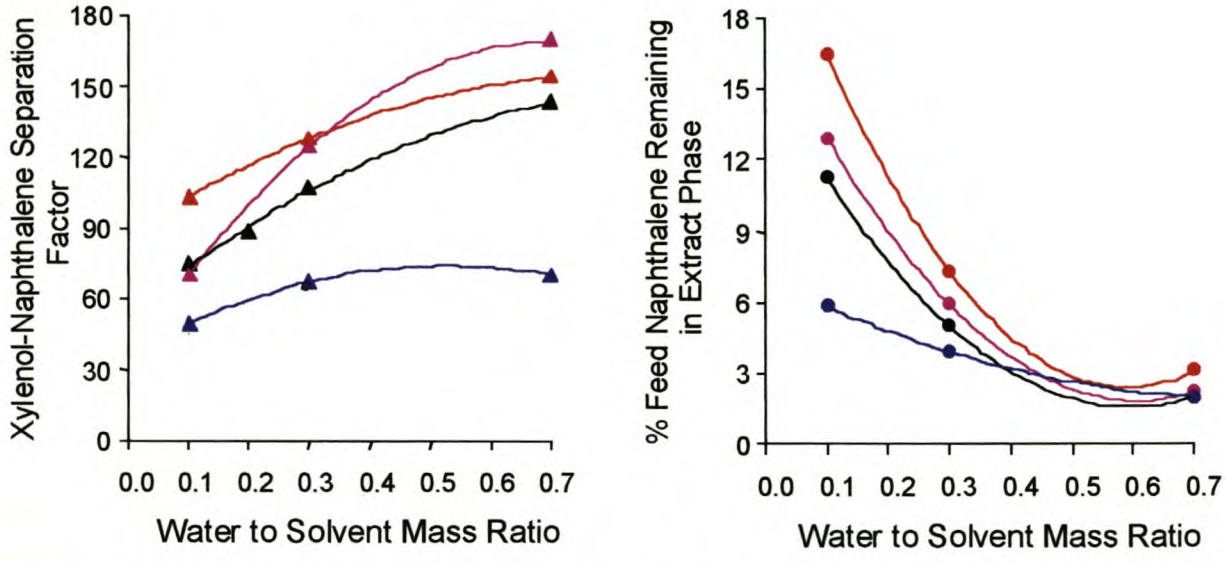


Figure 5.4-26. Effect of water to solvent mass ratio on the xylenol - naphthalene separation factor and the percentage of feed naphthalene remaining in the extract phase at a constant hexane to feed mass ratio of 5.0.

Xylenol-Naphthalene separation factor: ▲ S/F=0.5 ▲ S/F=1.5 ▲ S/F=2.0 ▲ S/F=3.0

Naphthalene recovery : ● S/F=0.5 ● S/F=1.5 ● S/F=2.0 ● S/F=3.0

From Figure 5.4-27 it can be seen that an increase in the hexane to feed ratio leads to decrease in the amount of naphthalene remaining in the solvent phase and to a corresponding increase in the xylenol - naphthalene separation factor. This can be attributed to the fact that the potential for naphthalene molecules to dissolve in the hexane phase increases as the ratio of hexane to naphthalene increases.

From Figure 5.4-25, Figure 5.4-26 and Figure 5.4-27 it can be concluded that it is only at very low hexane to feed ratios, combined with high solvent to feed ratios and very low water to feed ratios that the percentage of feed naphthalene remaining in the solvent phase is significant. At the combination of solvent ratios optimum for the separation of phenolic compounds from neutral oils, the separation of the phenolic compounds from naphthalene should be trivial.

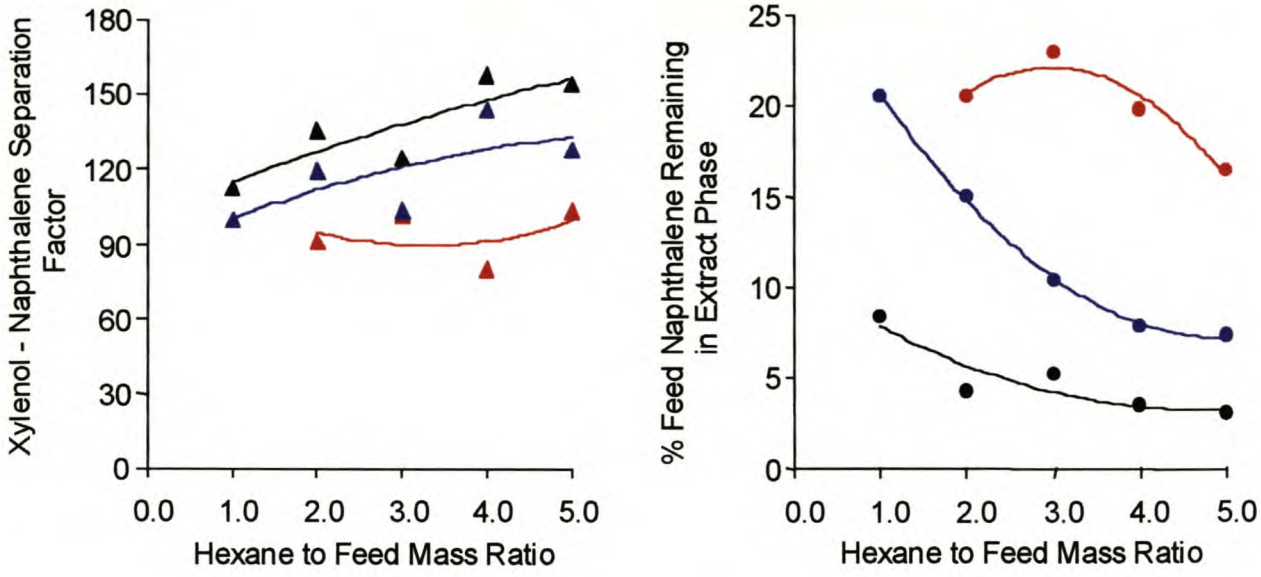


Figure 5.4-27. Effect of hexane to feed mass ratio xylenol - naphthalene separation factors and naphthalene recovery at a constant solvent to feed mass ratio of 3.0.

Xylenol - naphthalene separation factor: ▲ **W/S=0.67** ▲ **W/S=0.3** ▲ **W/S=0.1**

Naphthalene recovery: ● **W/S=0.67** ● **W/S=0.3** ● **W/S=0.1**

5.4.7 Separation of Phenolic Compounds from Indane and Indene

It can be seen from Table 5-10 that the values obtained for the xylenol-indane separation factor are very high and range from 49.7 to 2950. The percentage of indane remaining in the solvent phase ranges from 0.1% to 11.0%. It can thus be concluded that the separation of xylenol from indane is trivial.

The m-cresol-indene separation factors, while lower than the xylenol-indane separation factors are still very high, ranging from 26.5 to 381 (see Table 5-7). The percentage of feed indene remaining in the solvent phase is significantly higher than that of indane and ranges from 2.7 to 58.1%.

Indane and indene differ solely in the respect that indene has one more double bond than indene. Judging from this fact and the fact that the recovery of naphthalene is also substantially higher than that of indane, it can be concluded that unsaturated carbon bonds in a molecule heighten the affinity of that molecule for triethylene glycol. This is attributed to the fact a single-bonded carbon pair is bonded solely by means of a σ-bond, while a double-bonded carbon pair is bonded by both a σ-bond and a π-bond.

Thus, an unsaturated carbon bond contains a π-bond while a saturated carbon bond does not. In π-bonding, electron density is not along the axis connecting the two bonded atoms, rather it is above and below the axis [85]. The π bond is therefore capable of forming weak associations with the hydrogen of the hydroxyl functional group, in much the same way as the unbonded electron pairs of the nitrogen atoms of the amine functional group does. Obviously the association between a π-bond and a hydroxyl group is far weaker than the hydrogen bonds formed between two hydroxyl groups or an amine group and a hydroxyl group. It is however strong enough to cause indene and naphthalene, which have more unsaturated carbon bonds than indane, to have a higher affinity for triethylene glycol than does indane.

The effect of the solvent to feed ratio on m-cresol – indene separation factors and the percentage of feed indene remaining in the solvent phase is illustrated in Figure 5.4-28.

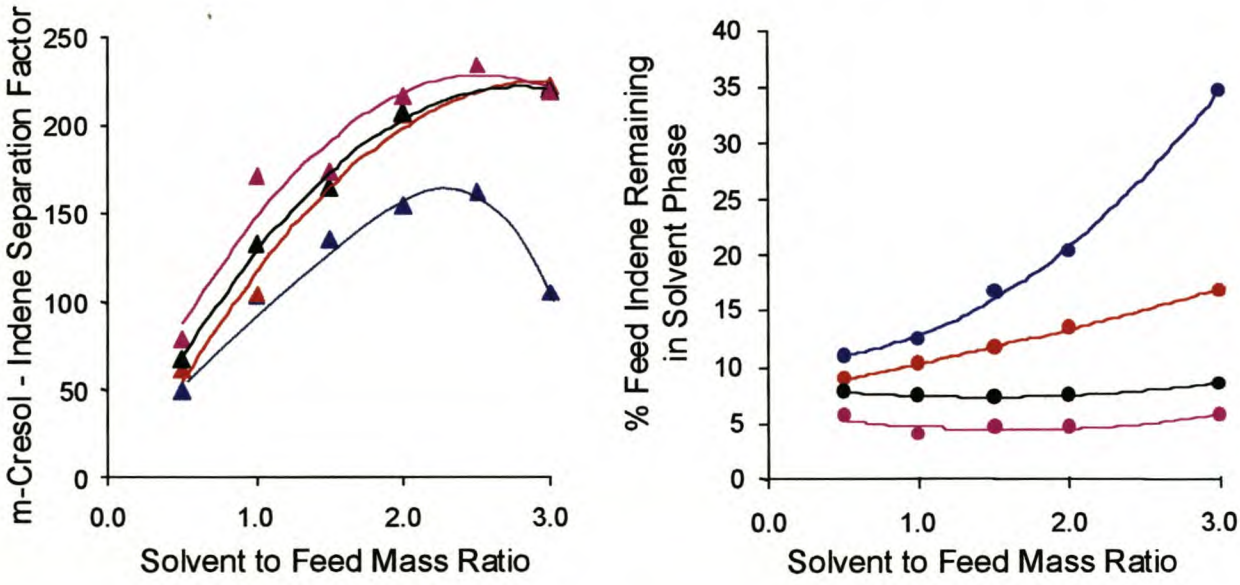


Figure 5.4-28 Effect of solvent to feed mass ratio on the m-cresol - indene separation factor and percentage of feed indene remaining in the extract phase at a constant hexane to feed mass ratio = 5.0.

m-Cresol-Indene separation factor: ▲W/S=0.67 ▲ W/S=0.3 ▲ W/S=0.1 ▲ W/S=0.0

Indene recovery : ●W/S=0.67 ● W/S=0.3 ●W/S=0.1 ● W/S=0.0

It can be seen from Figure 5.4-28 that, at a constant hexane to feed ratio of 5.0, at low water to solvent ratios of 0.0 and 0.1, the indene recovery increases with an increase in the solvent to feed ratio. At high water to solvent ratios of 0.3 and 0.67, an increase in the solvent to feed ratio does not lead to any noticeable increase in indene recovery. In fact, at a water to solvent ratio of 0.3, an initial increase in the solvent to feed ratio from 0.5 to 2.0 causes the indene recovery to decrease from 7.7 to 7.2%. A further increase in the solvent to feed ratio from 2.0 to 3.0 causes the indene recovery to increase to 8.4%. A similar trend is observed at a water to solvent ratio of 0.67.

It can therefore be concluded that the solubility of indene in the solvent phase is decreased by an increase in the water to solvent ratio. An increase in the solvent to feed ratio therefore has a smaller effect on the indene recovery at low water to solvent ratios than at high water to solvent ratios.

At a water to solvent ratio of 0.0, the increase in indene recovery with an increase in the solvent to feed ratio is significant enough that the m-cresol – indene separation factor decreases as the solvent to feed ratio increases from 2.0 to 3.0. At all other water to solvent ratios, the increase in indene recovery is successfully counteracted by the corresponding increase in the m-cresol recovery with an increase in solvent to feed ratio. This results in an increase in the m-cresol – indene separation factor.

The effect of the water to solvent ratio on indene recovery and the m-cresol – indene separation factor is illustrated in Figure 5.4-29.

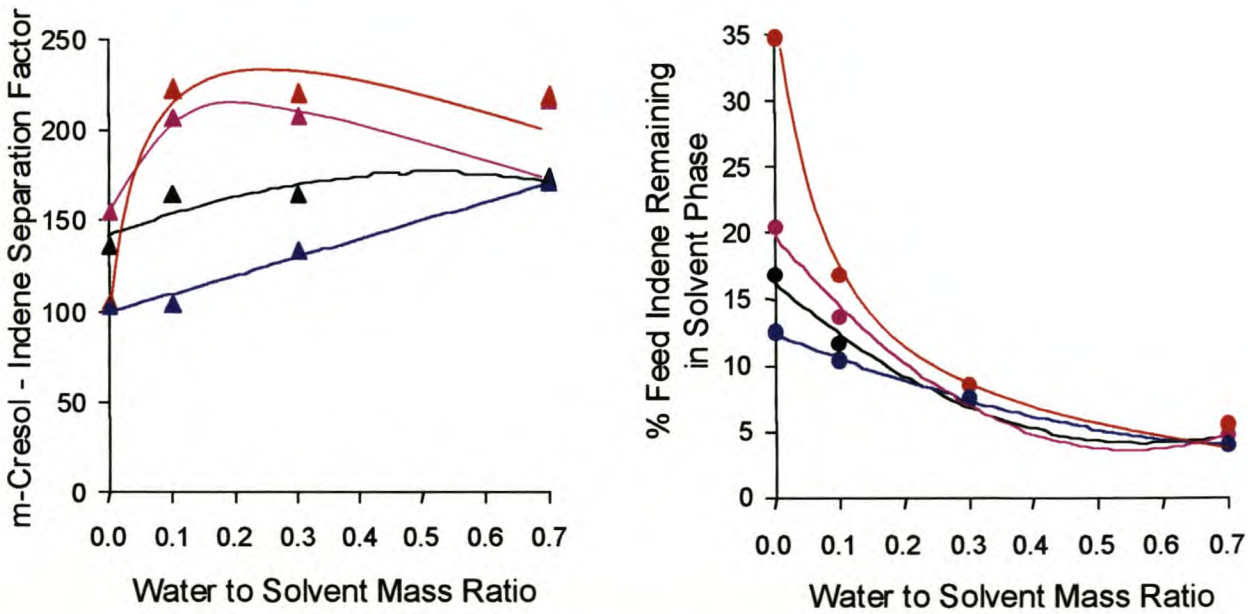


Figure 5.4-29. Effect of water to solvent mass ratio on the m-cresol - indene separation factor and the percentage of feed indene remaining in the extract phase at a constant hexane to feed mass ratio of 5.0.

m-Cresol - Indene separation factor: ▲ S/F=0.5 ▲ S/F=1.5 ▲ S/F=2.0 ▲ S/F=3.0

Indene recovery : ● S/F=0.5 ● S/F=1.5 ● S/F=2.0 ● S/F=3.0

Figure 5.4-29 confirms that the increase in the water to solvent ratio decreases the percentage of indene remaining in the solvent phase. The decrease is most significant at a solvent to feed ratio of 3.0. This can be attributed to the fact that the initial recovery of indene is much higher at a solvent to feed ratio of 3.0 than it is at other solvent to feed ratios. It should also be noted that while the initial recovery of indene is 34.6% at a solvent to feed ratio of 3.0, 20.3% at a solvent to feed ratio of 2.0 and only 12.5% at a solvent to feed ratio of 0.5, the final indene recoveries as the water to solvent ratio is

increased from 0.0 to 0.67 are all within the range 3.9 to 5.5%. It can therefore be concluded that there is a limit to the amount of indene that can be removed from the solvent phase by increasing the water to solvent ratios alone.

It can be seen in Figure 5.4-26 that the same trend is exhibited by the naphthalene recovery.

The effect of the hexane to feed ratio on indene recovery and m-cresol – indene separation factors is illustrated in Figure 5.4-30.

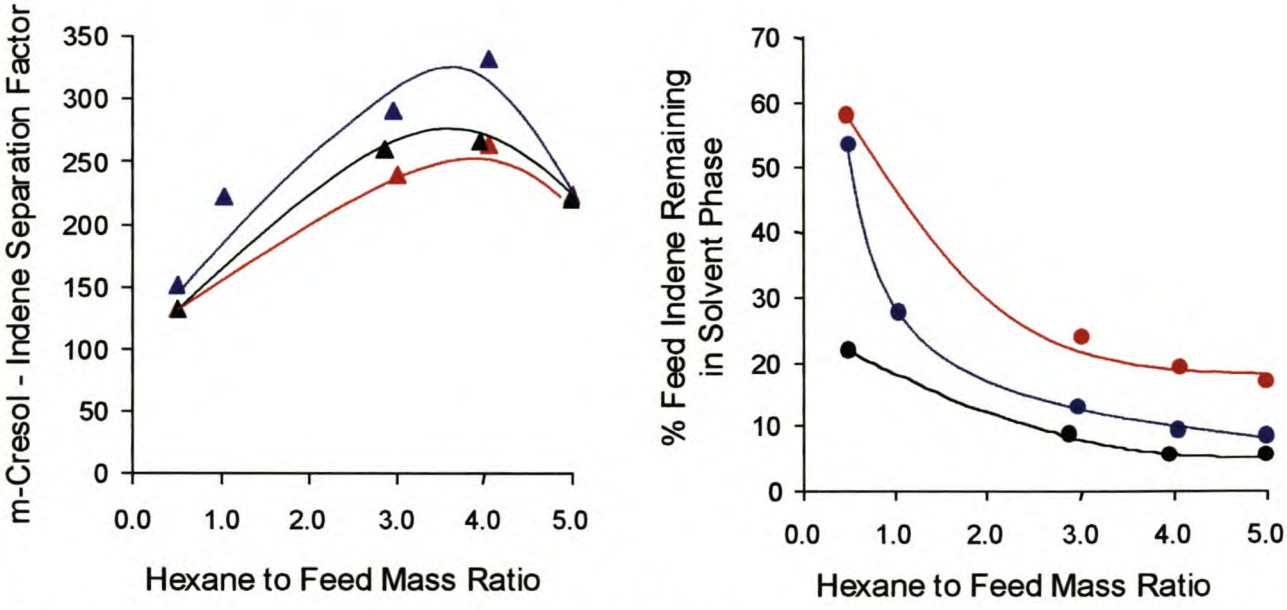


Figure 5.4-30 Effect of hexane to feed mass ratio m-cresol - indene separation factors and indene recovery at a constant solvent to feed mass ratio of 3.0.

m-Cresol - indene separation factor: ▲ **W/S=0.67** ▲ **W/S=0.3** ▲ **W/S=0.1**

Indene recovery: ● **W/S=0.67** ● **W/S=0.3** ● **W/S=0.1**

The effect of an increase in the hexane to feed ratio on the recovery of indene is analogous to the effect of an increase in the water to solvent ratio. It can be seen from Figure 5.4-30 that an increase in the hexane to feed ratio beyond a value of 4.0 leads to a decrease in the m-cresol – indene separation factor. This can be attributed to the fact that the decrease in indene recovery is negligible as the hexane to feed ratio is increased from 4.0 to 5.0. The slight decrease in m-cresol recovery therefore causes the decrease in the separation factor.

As with naphthalene, the percentage of indene remaining in the solvent phase is only significant at low hexane to feed ratios combined with high solvent ratios and low water to solvent ratios.

5.4.8 Optimum solvent ratios

The effect of the various solvent ratios can be concluded as follows:

Solvent to feed ratio:

- An increase in the solvent to feed ratio leads to an increase in the recovery of phenolic compounds, nitrogen bases and neutral oils.
- The increase is more significant at low water to solvent ratios than at high water to solvent ratios.
- An increase in the phenolic recovery with an increase in solvent to feed ratio is most significant at high hexane to feed ratios.
- The separation factors pertaining to phenolic compounds and nitrogen bases as well as those pertaining to phenolic compounds and neutral oils increase with an increase in the solvent to feed ratio, i.e. the increase in the phenolic compound recovery successfully counteracts the corresponding increase in nitrogen base and neutral oil recovery.
- An increase in the solvent to feed ratio beyond 3.0 does not result in any significant increase in phenolic recovery.

Water to solvent ratio:

- An increase in the water to solvent ratio leads to a decrease in the recovery of phenolic compounds, nitrogen bases and neutral oils
- Xylenol isomers, in particular 2,4-xylenol, are more sensitive to an increase in the water to solvent ratio than either m-cresol or phenol
- The recovery of the xylenol isomers decreases sharply at water to solvent ratios in excess of 0.3
- The optimum water to solvent recoveries for the separation of phenolic compounds from nitrogen bases is 0.1. The effect of the decrease in phenolic recovery with an increase in the water to solvent ratio was determined to have a disproportionately large effect on the separation factors. As such a higher water to solvent ratio is justified for the removal of nitrogen bases from the extract phase
- Very low water to solvent ratios (<0.1) should not be used in conjunction with very low hexane to feed ratios (<0.5) and high solvent to feed ratios (>2.0) as the percentage of feed neutral oils remaining in the extract phase becomes significant in this solvent region.

Effect of the hexane to feed ratio

- An increase in the hexane to feed ratio leads to a decrease in the recovery of phenolic compounds, nitrogen bases and neutral oils.
- The effect of the hexane to feed ratio on phenolic recovery is most significant at high water to solvent ratios (>0.3).
- The decrease in phenolic recovery as the hexane to feed ratio is increased from 3.0 to 5.0 is not very large. The higher hexane to feed ratio is thus justified for the removal of nitrogen bases and neutral oils from the extract phase.
- The separation of phenolic compounds from nitrogen bases is more favourable as the hexane to feed ratio is increased. The optimum hexane to feed ratio for phenol-benzonitrile, phenol - 5-et-2-me-pyridine and phenol - aniline separation factors is 5.0. The optimum hexane to feed ratio for m-cresol - o-toluidine and m-cresol - o-tolunitrile separation factors is 3.0. As the separation of the phenol from aniline and benzonitrile is more difficult than that of m-cresol from o-tolunitrile and o-toluidine, the optimum hexane to feed ratio for the former separation, i.e. 5.0, is preferred.

The optimum solvent ratios are therefore

- Solvent to feed : 3.0
- Water to solvent : < 0.2
- Hexane to feed : 5.0

Having determined the optimum solvent to feed, hexane to feed and water to solvent ratios for a single-stage extraction process using the proposed solvent system, the next step in the development of the desired separation process is the optimisation of a multistage extraction process. The optimum single-stage solvent ratios can be used as a starting point in the determination of the optimum solvent ratios for a multistage process. As multistage pilot plant tests are time-consuming and require large volumes of chemicals, it is preferable that they be supplemented with simulations based on a thermodynamic model. An appropriate thermodynamic model must therefore be obtained through the regression of the LLE data generated with the batch extraction tests. The development of such a model is discussed in the following chapter.

CHAPTER 6. THERMODYNAMIC MODELLING

6.1 Introduction

In designing a separation process, an understanding of the required phase equilibria is essential. Ideally, this should be based on reliable experimental data for the mixture under investigation and parameters such as temperature, pressure and composition should correspond to those required for the desired separation process.

Unfortunately, applicable experimental data are seldom available. This is especially true for liquid-liquid systems. The possible number of liquid and vapour mixtures that are of interest in technological processes is huge. Furthermore, the generation of good experimental data requires skill and is time-consuming. The consideration of techniques whereby the limited data at hand can be reduced and correlated to make the best possible interpolations and extrapolations is therefore an economic necessity.

Liquid-liquid equilibria, like vapour liquid equilibria, depend on the nature of the components present, on their concentrations in both phases and on the temperature of the system. Multicomponent equilibria are determined by a large number of variables. An efficient organisational tool is therefore needed to reduce available experimental data to a small number of theoretically significant functions and parameters, which can then be used as building blocks for the construction of the desired equilibria.

Thermodynamic analysis and synthesis provides such an organisational tool. Firstly, limited pure component and binary data are analysed to yield fundamental thermodynamic quantities. These quantities are then reduced to obtain parameters in a molecular model. The model may then be used to calculate the phase behaviour of multicomponent liquid and vapour mixtures.

6.2 Theory

For a multicomponent two-phase liquid-liquid extraction system, the activities of each component in both phases must be equal. The equations of equilibrium that must be satisfied are therefore of the form:

$$\gamma^{I}_{i}\, x^{I}_{i} = \gamma^{II}_{i}\, x^{II}_{i} \qquad (6.2\text{-}1)$$

where γ^{I}_{i} and γ^{II}_{i} are the activity coefficients of component i in the extract and raffinate phases respectively. The activity coefficients are a function of the temperature and concentration of each of the n species in the respective phases [81].

There are k equations of the form shown in Equation 6.2-1, where k is the number of components in the system. Once these functions are established, the problem is in principle solved.

Two models that are specifically aimed at predicting liquid activity coefficients are the UNIQUAC and NRTL (Non-Random Two Liquid) models. The UNIQUAC model could not be applied to the extraction system under investigation due to the absence of published area and volume parameters for the aromatic amines. The NRTL model was therefore used as a basis for modelling.

The three parameter version of the NRTL equation is as follows [81]:

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left[\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k G_{kj} x_k} \right] \qquad (6.2\text{-}2)$$

$$\tau_{ij} = \frac{b_{ij}}{T} \qquad (6.2\text{-}3)$$

$$G_{ij} = \exp\left(-\alpha_{ji} \tau_{ji}\right) \qquad (6.2\text{-}4)$$

α_{ij} is assumed to be equal to α_{ji} and is typically assigned a value of 0.2. The activity coefficient of a component in a specific phase can thus be predicted if the binary parameters b_{ij} and b_{ji} are known for each pair of components in the multicomponent system.

Binary liquid-liquid parameters for a limited number of component pairs are found in the literature. Those that are not can be estimated very roughly by reduction of vapour-liquid equilibrium (VLE) data or determined through regression of experimental equilibrium data.

It has already been mentioned in Section 3.3. that parameters obtained by the reduction of VLE data mostly fail to predict liquid-liquid equilibria accurately. Therefore, wherever possible, parameters should be obtained from liquid-liquid equilibria (LLE) data. Even

then it is difficult to obtain a truly unique set of parameters, even for data of high experimental accuracy. There is typically a range of parameter sets and any set in that range could equally well reproduce the experimental error. Unlike calculated VLE data, calculated LLE data are extremely sensitive to the choice of binary parameters [81].

Therefore, it is difficult to model ternary or higher liquid-liquid equilibria by using only binary parameters obtained from binary LLE and VLE data. For reliable results it is necessary to utilise at least some multicomponent LLE data. The multicomponent equilibrium data generated by the batch extraction tests are therefore an ideal source of data for the determination of binary parameters for the modelling of the proposed separation system.

The distribution coefficient for a component i between two liquid phases was defined in Section 3.3 as:

$$K_i = x^{I}_i / x^{II}_i \qquad (3.3\text{-}1)$$

By combining Equations 3.3-1 and 6.3-1:

$$K_i = \gamma^{II}_i / \gamma^{I}_i \qquad (6.2\text{-}5)$$

The values of $x^{I}_i \ldots x^{I}_n$ and $x^{II}_i \ldots x^{II}_n$ are known from experimental equilibrium data. Experimental K values can therefore be calculated for each of the k components for each experimental point.

Similarly, the equilibrium compositions of the k components present in the multicomponent extraction system can be substituted into the NRTL equation. Assuming $\alpha = 0.2$, the activity coefficients $\gamma^{I}_i \ldots \gamma^{I}_n$ and $\gamma^{II}_i \ldots \gamma^{II}_n$ for each experimental point can now be expressed as functions of the binary parameters b_{ij} and b_{ji}. A theoretical distribution coefficient, which is a function of the binary parameters, can then be obtained by substituting the NRTL activity coefficients into Equation 6.2-5.

The binary parameters are therefore the only unknowns and can be determined by means of iterative regression techniques.

In VLE it is relatively easy to start the iteration because assumption of ideal behaviour (Raoult's Law) provides a reasonable initial approximation. By contrast, there is no obvious corresponding method to start the iteration calculation for LLE. When two liquid phases are present, the activity coefficients in both phases must be calculated. Since these are strongly non-linear functions of compositions, LLE calculations are highly sensitive to small changes in composition. In VLE at modest pressures, this sensitivity

is lower because vapour phase fugacity coefficients are usually close to unity and only weak functions of composition. For LLE, it is therefore more difficult to construct a numerical iteration procedure that converges both rapidly and consistently [81].

6.3 Relevance and Application to System under Investigation

Optimum solvent ratios have been determined for the proposed solvent system with regards to the recovery of phenolic compounds and the separation thereof from a range of neutral oils and nitrogen bases. However, these optimum solvent ratios are based on a single extraction step only. I.e. the optimum conditions for multistage separation are not known. The equilibrium data obtained from the batch extractions can however assist in predicting the best theoretical multistage separation conditions. This would narrow the range of operating conditions to be tested on pilot plant scale and assist in the assessment of the performance of the pilot plant.

Firstly, binary parameters for the NRTL model can be determined through regression of the batch extraction equilibrium data. The thermodynamic model based on these parameters can then be used in simulations to predict the composition of phenolic compounds, neutral oils and nitrogen bases for each stage of a multistage extraction column.

The validity of the results obtained by means of simulations with a specific model must first be tested against known experimental batch extraction data before the model can be used in further multistage simulations.

For reasons discussed in Chapter 7, the synthetic feed stream used for testing the proposed solvent system on pilot plant scale consists of a mixture of m-cresol, p-cresol, o-tolunitrile and aniline. Triethylene glycol is used as the solvent, water as the co-solvent and hexane as the countersolvent. The multicomponent system that must ultimately be modelled is therefore: hexane + water + aniline + o-tolunitrile + m-cresol + p-cresol + triethylene glycol.

The equilibrium data that is most applicable to the pilot plant multicomponent mixture are those generated by the extractions performed on the m-cresol feed stream. As two binary parameters are required for each pair of components in a multicomponent mixture, and as the LLE system applicable to the m-cresol feed stream contains nine components, 72 binary parameters are required to model the system. I.e. the system must be optimised in 72 dimensions.

The number of parameters to be determined can be reduced by using published binary parameters, where available. Unfortunately, very few LLE binary parameters are available in the literature. In the case of the m-cresol system, only 2 pairs of published binary parameters were found: those for the m-cresol-water and water-hexane component pairs. I.e. 68 binary parameters remain to be determined. The problem set to the regression algorithm would be simplified if additional parameters could be established.

The component pairs hexane-triethylene glycol, hexane-water and water-triethylene glycol are common to the three LLE systems generated with the phenol, m-cresol and xylenol feed streams. These LLE systems will respectively be referred to as the phenol, m-cresol and xylenol systems in further discussion. The hexane-triethylene glycol, hexane-water and water-triethylene glycol binary parameters determined for one of the systems under investigation can therefore be used in the modelling of the other two systems.

Where the m-cresol system contains nine components, the phenol system contains only eight. I.e. 56 binary parameters are required to model the system. Also, four pairs of binary parameters applicable to the phenol system are available in the literature, namely those for the water-hexane, water-phenol, water-aniline and hexane-aniline component pairs. Therefore, only 52 binary parameters remain to be determined. Optimisation of the phenol system is clearly simpler than optimisation of the m-cresol system and, consequently, the phenol system was optimised first. The parameters obtained for the hexane-triethylene glycol, hexane-water and water-triethylene glycol component pairs could then be used in the optimisation of the m-cresol system. In this way, the number of parameters to be determined in the m-cresol system was decreased from 68 to 62.

Two further series of batch extractions were executed in order to generate LLE data for the modelling of the pilot plant LLE system. The first series was executed on a feed stream consisting of m-cresol, p-cresol and o-tolunitrile in order to generate LLE data for the determination of binary parameters applicable to p-cresol. I.e. LLE data for the system hexane + water + o-tolunitrile + m-cresol + p-cresol + triethylene glycol was generated at temperature of 40°C. The feed compositions for this series of batch extractions as well as the corresponding compositions of the resulting liquid phases are listed in Appendix A6.

Of the 30 binary parameters required to model this six component system, 20 were already determined for the m-cresol nine component system. Thus, only 10 parameters, those for the component pairs containing p-cresol, remained to be determined.

The second additional dataset was generated for the determination of binary parameters applicable to aniline. This system consisted of the components hexane + water + aniline + o-tolunitrile + m-cresol + p-cresol + triethylene glycol. The feed compositions and compositions of the resulting liquid phases for this system are listed in Appendix A7. Binary parameters for aniline-hexane, aniline-water and aniline-triethylene glycol were previously determined for the eight-component phenol system. The only unknown binary parameters still to be determined were those for the aniline - o-tolunitrile, aniline - m-cresol and aniline - p-cresol component pairs.

In this way, the binary parameters required for the modelling of the pilot plant LLE system were determined.

The LLE system applicable to the xylenol feed stream, i.e. the system hexane + water + indane + dodecane + naphthalene + 2,4-xylenol + 3,5-xylenol + 3,4-xylenol + triethylene glycol, was also modelled. In this system the parameters for hexane - water, hexane - triethylene glycol and water - triethylene glycol were the same as those determined with the phenol multicomponent system. Of the 72 parameters required to model this nine component system, 6 were already known. Thus 66 remained to be determined.

A system derived from the phenol system, in which triethylene glycol monomethylether replaced triethylene glycol as a solvent in the phenol system, was also modelled in order to test the validity of the parameters determined by regression of the phenol system. There is always a possibility that the parameters determined with a regression algorithm may not be the true optimum parameters, especially if the regression algorithm is susceptible to local minima traps. These parameters are seldom applicable to systems that differ from those for which they were determined. If the parameters determined for the system containing triethylene glycol are inapplicable to the system containing triethylene glycol monomethylether, it can be concluded that the parameters are not the true optimum parameters.

6.4 Regression Algorithm

The modelling of the systems under investigation is complicated by the highly uneven distribution of components between the two phases. E.g. in the phenol system, four of the eight components (hexane, water, mesitylene and triethylene glycol) are practically insoluble in one of the phases, and a fifth, phenol, is to all intents and purposes present only in the solvent phase. Also, the three components that are more evenly distributed between the two phases, namely 5-et-2-me-pyridine, benzonitrile and aniline, are present in small amounts. The antisolvent phase therefore consists almost exclusively of hexane.

The m-cresol and xylenol systems are subject the same complication.

Most regression techniques rely on the minimisation of an error sum. In the case of regression of LLE data, the errors to be minimised are typically the differences between experimental and theoretical distribution factors. The distribution factors are the molar fraction of a component in the solvent phase (x^{I}_{i}) divided by the molar fracion of that same component in the antisolvent phase (x^{II}_{i}). In the phenol system, six of the eight components have extremely small concentrations in the antisolvent phase. I.e. the value of x^{II}_{i} for these components is small and the value of K_i is consequently very large. Also, very small fluctuations in the value of x^{II}_{i} lead to very large fluctuations in the value of K_i. The values of the errors generated as a result are disproportionately large.

From the results of the batch extraction tests it can be concluded that the component concentrations that are most important are those of phenol, aniline, benzonitrile, 5-et-2-me-pyridine, and mesitylene. These components have concentrations in the hexane phase which, while very small in comparison to hexane, are orders of magnitude larger than those of water and triethylene glycol. I.e. their distribution factors are considerably smaller than those of water and triethylene glycol and, consequently, the error values generated are not as large. Standard regression techniques would thus place more emphasis on minimising the larger errors applicable to triethylene glycol and water than to those applicable to phenol, the nitrogen bases and mesitylene.

An added complication is that the available pairs of published binary parameters were determined using binary LLE data. There is no guarantee that these parameters are the true optimum parameters for the reported components and do not correspond to local minima in the solution space of possible parameters.

The factors that must be addressed when selecting a regression technique are thus:

1. the typical error sum to be minimised is susceptible to disproportionately large fluctuations with small changes in the parameters to be optimised;
2. the accurate prediction of the concentrations of phenolic compounds and nitrogen bases must be emphasised;
3. the NRTL equation is extremely non-linear;
4. most regression techniques are susceptible to local minima traps;
5. initial estimates for the binary parameters are poor;
6. available published binary parameters are not guaranteed to be the true optimum parameters for the reported component pairs.

A non-linear regression algorithm which is relatively independent of the initial values chosen and which has an objective function that can be altered so as to favour the

prediction of certain components, is thus required. Published parameters are not fixed, but are used as initial values for the regression algorithm.

A program, NRTLFit, developed in the Institute for Thermal Separations (University of Stellenbosch) was used for regression [86]. This program incorporates a particle swarm method [87], the Levenberg-Marquardt regression algorithm [88] and flash calculations to arrive at the optimum binary parameters.

6.4.1 Particle swarm method

In the particle swarm method, a search space is defined for the parameters to be optimised. A number of initial starting positions, or particles, are randomly selected in this search space. A particle is essentially a vector consisting of as many dimensions as there are dimensions in the search space, which is assigned a random weight and velocity [87], [89]. Each particle is then evaluated, i.e. the values for each parameter to be optimised, at the position of the particle in the search space, are substituted into the goal function and the error sum is calculated . The velocity of each particle is then changed according to an equation of the form [90]:

$$V^{k+1} = W_o \times randg_1(m_1,\sigma_1) \times V^k + w_1 \times (PB-CP) + w_2 \times (GB-CP) + randg_2(m_2,\sigma_2) \quad (6.4\text{-}1)$$

where

V^k and V^{k+1}	:	velocites of the particle at time-steps k and k+1
W_o	:	inertia of the particle
w_1, w_2,	:	uniformly distributed random values between 0 and 2
$randg_1$ and $randg_2$	:	random values with a gaussian distribution
m_1 and σ_1	:	median and standard deviation applicable to $randg_1$
m_2 and σ_2	:	median and standard deviation applicable to $randg_2$
PB	:	personal best position of the particle
CP	:	current position of the particle
GB	:	global best position of all the particles in the swarm

The inertia of the particle, W_0, is diminished with each time-step. The start and end inertia for a regression can be specified. m_1 and σ_1 are assigned fixed values of 0.5 and 0.7 respectively. m_2 and σ_2 are assigned values of 0.0 and 0.01 respectively. The number of particles can be specified for each regression, as can the number of time-steps and number of times the regression must be repeated.

The parameters available in the literature were used as initial values for the regression. The range over which each parameter could vary was specified.

The goal function was defined as follows:

$$F = \sum_i w_i \varepsilon_i^2 \qquad (6.4\text{-}2)$$

where

F	:	goal function to be minimised
w_i	:	user-specified weight assigned for component i
ε_i	:	error term for component i and is defined as:

The error term for each component, ε_i ,is defined in such a way as to minimise the effect of small concentrations of components in one of the two liquid phases:

$$\varepsilon_i = \frac{\gamma_i^I x_i^I - \gamma_i^{II} x_i^{II}}{\frac{1}{2}\left(\gamma_i^I x_i^I + \gamma_i^{II} x_i^{II}\right)} x100 \qquad (6.4\text{-}3)$$

The weight, w_i, can be varied to emphasise specific components.

The algorithm can be summarised as follows:

1. The search space is defined by specifying a minimum and maximum value allowed for each binary parameter.
2. A specified number of particles are randomly selected within the search space.
3. γ^I_i and γ^{II}_i for each component are calculated for each particle with the NRTL equation, using the experimental molar fractions and binary parameters applicable to the particle in question.
4. The error function is calculated for each particle using the applicable calculated γ^I_i and γ^{II}_i values and experimental molar fractions.
5. The position of each particle in the search space is changed, based on the value of the error function for the particle and that of all the other particles in the swarm using Equation 6.4-1.
6. Steps 3 to 5 are repeated a specified number of times.

The algorithm is repeated until the error function is minimised. The optimum set of binary parameters obtained for each regression can be used as the set of initial values for the next regression.

The optimum parameters obtained with the particle swarm method are used as initial values for further regression with the Levenberg-Marquardt algorithm.

6.4.2 Levenberg-Marquardt Algorithm

Most algorithms for the non-linear least-squares estimation of parameters centre about one of two approaches. The model may be expanded as a Taylor series or a modification of the steepest-descent method may be used. Both methods have inherent disadvantages. Divergence of successive iterations may cause the Taylor series to fail, while the steepest-descent methods are subject to slow convergence after the first few iterations [88].

The Levenberg-Marquardt algorithm is an extension of the Newton method to allow for convergence with relatively poor starting estimates for the unknown coefficients. A least squares objective function is utilised. In this method, the Newton normal equations are modified by adding a factor λ.

$$[\mathbf{A}^T\mathbf{A} + \lambda \times \mathbf{I}] \times \Delta\mathbf{A}^* = \mathbf{A}^T \times (Y - Y^*) \qquad (6.4\text{-}4)$$

where

A :	matrix of first derivatives of the objective function with respect to the adjustable parameters
$\Delta\mathbf{A}^*$:	parameter difference matrix
Y :	specified output parameter
Y* :	predicted output parameter
I :	identity matrix

I.e., λ is added to each term of the main diagonal of the $\mathbf{A}^T\mathbf{A}$ matrix. When λ approaches $+\infty$, this method is identical to the Steepest Descent method. When λ equals zero, the method reduces to Newton. In the Marquardt procedure, the initial values of λ are large and will decrease toward zero as the optimum is approached. In this way, the ability of the Steepest Descent method to converge for poor starting values and the rapid convergence of the Newton method are combined. The rules for

calculating λ are discussed in the original article by Marquardt [88]. All other computational details are identical to those used in the standard Newton procedure.

The goal function for the Levenberg-Marquardt algorithm is the same as that defined for the Particle Swarm Method.

6.4.3 Flash Algorithm

The optimum parameters obtained with the Particle swarm method in combination with the Levenberg – Marquardt method, as described above, are used as starting values for further regression.

Further regression is by means of the same particle swarm approach as before, but the error function is changed in order to obtain a more accurate fit, based on the actual molar fractions of the various components in the system in both phases, rather than on a ratio of molar fractions.

Thus :

$$F = \sum_i w_i \varepsilon_i^2 \qquad (6.4\text{-}5)$$

where the error term for each component is defined as:

$$\varepsilon_i = \frac{\left| x_i^{I,flash} - x_i^{I,exp} \right|}{x_i^{I,exp}} + \frac{\left| x_i^{II,flash} - x_i^{II,exp} \right|}{x_i^{II,exp}} \qquad (6.4\text{-}6)$$

$x_i^{I,flash}$ and $x_i^{II,flash}$ are calculated for each time-step of the particle swarm with a Rachford and Rice flash algorithm [91] using the NRTL equation. The parameters used in the NRTL equation are those under evaluation for the particular time-step.

The algorithm for this stage of the regression is a follows

1. The search space is defined by specifying a minimum and maximum value allowed for each binary parameter.
2. A specified number of particles are randomly selected within the search space.
3. x^{I}_{i} and x^{II}_{i} are calculated for each component with a flash algorithm using the NRTL equation as function of the binary parameters applicable to the particle under evaluation.
4. The error function is calculated using the calculated x^{I}_{i} and x^{II}_{i} values and experimental molar fractions for each particle.
5. Based on the error function for the particle under evaluation, as well as the error function of all the particles in the swarm, position of each particle in the search space is changed (using equation 6.4-1)
6. Step3 to 5 are repeated a specified number of times..

Once the optimum parameters have been determined with the particle swarm method and the modified goal function, they are used as starting values for further regression with the Levenberg-Marquardt algorithm. The algorithm is identical to that used previously, except that the error terms in the goal function are as defined in Equation 6.4-6.

It was mentioned in Section 6.3 that it is possible that the binary parameters obtained through regression may not be the true optimum binary parameters for the system under investigation, but may correspond to local minima in the regression solution space. Very few binary parameters applicable to the systems under investigation have been published and these were published in 1979 [92]. Given the fact that regression techniques have improved considerably in the last 20 years, there is no guarantee that the published binary parameters are in fact the optimum parameters for the applicable component pairs. As such, these binary parameters were used only as initial values and not as fixed parameters.

Apart from the published binary parameter values, the initial values for the particle swarm method which was used to minimise the goal function in Equation 6.4-3 were randomly selected. In order to ensure that the global optimum within the solution space was obtained, this algorithm was executed numerous times with different sets of randomly selected initial values. Each time the algorithm converged to a set of binary parameters that varied over a narrow range of values. It could therefore be concluded that the global optimum for the regression solution space lay within this range of values. The optimum set of parameters determined with the particle swarm method was then used as the initial values for the Levenberg-Marquardt algorithm. I.e. the initial values for the Levenberg-Marquardt algorithm were close to the global optimum values. Under

these conditions, the Levenberg-Marquardt algorithm is effective in determining the global optimum solution. It is important to note that the Levenberg-Marquardt algorithm on its own would be unlikely to determine the global minimum. The solution space for the particle swarm method based on the flash algorithm goal function was then limited to a narrow range of values bracketing the optimum set of binary parameters determined with the goal function in Equation 6.4-3. These optimum parameters were used as initial values for further regression.

It can therefore be concluded with reasonable certainty that the binary parameters obtained correspond to the global minimum in the regression solution space.

6.5 Simulation of Batch Tests.

The theoretical optimisation of the proposed solvent system with respect to multistage extraction is based on simulations, which are in turn based on the binary parameter sets determined for the NRTL model. The validity of the results generated with each proposed parameter set must therefore be evaluated with respect to known batch extraction experimental results, before the model can be accepted for use in the simulation of multistage extraction.

Each of the batch extraction tests in each series of batch extractions used to generate the original LLE data was therefore simulated using the appropriate proposed set of binary parameters. The simulation package used was ProII version 5.1 (Simulation Sciences Inc.). The batch extractions were modelled as isothermal flash unit operations. The mass composition of each simulation feed stream was specified as that of the corresponding experimental extraction feed mixture. The temperature and pressure were specified as being the same as for the batch extraction tests, namely 40°C and 101.3 kPa. The thermodynamic model used was the three parameter NRTL equation and the binary parameters were specified as those determined by regression of the generated multicomponent experimental LLE data.

The input file for batch extraction 1A is given in Appendix D1 .

6.6 Results

6.6.1 Phenol System

The optimum binary parameters determined for the phenol system, i.e. the eight-component liquid-liquid system hexane + water + mesitylene + 5-et-2-me-pyridine + aniline + benzonitrile + phenol + triethylene glycol, are shown in Table 6-1. These binary parameters were obtained through regression of the 89 LLE data points obtained from the batch extractions executed on the phenol feed stream. The weights applicable to the component error terms of the regression goal function were specified as follows: hexane, 0.05; water, 0.05; mesitylene, 0.05; 5-et-2-me-pyridine, 1.0; aniline, 1.0; benzonitrile, 1.0; phenol, 1.0 and triethylene glycol, 0.005. It was thus ensured that the large error terms expected for components sparingly soluble in one of the two liquid phases did not dominate the goal function. It was also ensured that the model would emphasise accurate prediction of the distribution of phenol and the nitrogen bases between the two liquid phases.

The batch extractions executed on the phenol feed stream were simulated using the parameters listed in Table 6-1 The simulated and corresponding experimental molar compositions of the resulting phases are listed in Appendix C1

Table 6-1. Optimum NRTL binary parameters for the system Hexane(1) + Water(2) + Mesitylene(3) + 5-Et-2-me-pyridine(4) + Aniline(5) + Benzonitrile(6) + Phenol(7) + Triethylene glycol(8). $\alpha_{ij} = \alpha_{ji} = 0.2$.

i	j	b_{ij}	b_{ji}	i	j	b_{ij}	b_{ji}
1	2	1883.5	3579.9	3	5	-139.9	6691.5
1	3	-1500.6	6366.4	3	6	1758.8	2330.3
1	4	2012.6	5960	3	7	-261.3	6656.4
1	5	481.5	503.2	3	8	1326.6	-1419
1	6	2233.4	-131.2	4	5	-955.2	1674.8
1	7	1019.9	84.91	4	6	2469.8	2340
1	8	2164.5	1559	4	7	1510.5	1105.1
2	3	351	750.5	4	8	2546.4	1440.1
2	4	2996.2	5230.9	5	6	1044	-129.9
2	5	950.4	62.63	5	7	1630	-709
2	6	2602.8	6205.8	5	8	278.6	-450.3
2	7	1403.2	-211.3	6	7	1057.7	996.5
2	8	-248	6668.6	6	8	3561	1335.6
3	4	1445.5	-199.3	7	8	-216.7	-267.6

The percentage errors between the simulated and experimental molar fractions of each component in the extract and hexane phase are listed in Table 6-2.

Table 6-2. Average, minimum and maximum percentage errors, ε_{Ave}, ε_{Min}, and ε_{Max}, between experimental and simulated molar fractions of components in the extract and hexane phases for the phenol system.

Components	Extract Phase			Hexane Phase		
	ε_{Ave} [%]	ε_{Min} [%]	ε_{Max}[%]	ε_{Ave} [%]	ε_{Min} [%]	ε_{Max}[%]
Hexane	50.5	1.9	290.6	0.5	0.0	3.8
Water	1.1	0.0	6.7	26.7	0.0	79.1
Mesitylene	24.6	2.5	88.7	4.4	0.0	25.6
5-Et-2-me-pyridine	4.6	0.1	22.1	5.6	0.0	20.6
Aniline	2.1	0.1	23.6	6.5	0.5	24.9
Benzonitrile	3.5	0.0	24.1	6.3	0.0	34.6
Phenol	1.8	0.0	20.0	10.8	0.1	43.7
Triethylene Glycol	1.6	0.0	8.0	82.9	10.0	162.2

It can be seen from Table 6-2 that, while the average percentage errors obtained between the simulated and experimental molar fractions for certain of the components in one of the two phases are acceptable, large maximum percentage errors are obtained for all the components in both phases. It could therefore be concluded that the results simulated with the NRTL equation differ significantly from the corresponding experimental results. These large percentage errors are however misleading. E.g. the maximum error obtained for the molar fraction of phenol in the extract phases is 20.0%. This error is applicable to a data point for which the simulated and experimental molar fractions of phenol in the extract phase are 0.117 and 0.147 respectively. I.e. the absolute difference between the predicted and actual percentage concentration of phenol in the extract phase is only 3.0 percentage points.

It can also be noted that the correlation between the simulated and experimental molar fractions of the feed components 5-et-2-me-pyridine, aniline, benzonitrile, and phenol in the hexane phase is noticeably less favourable than in the solvent phase. This is due to the fact that the combined molar fractions of the feed components, water and triethylene glycol in the hexane phase is on average less than 0.1. I.e. small deviations in the simulated and experimental molar fractions of these components in the hexane phase correspond to large percentage errors.

Similarly, very high percentage errors are obtained for the hexane and mesitylene molar fractions in the extract phase, as well as for the water and triethylene glycol molar fractions in the hexane phase. E.g. the maximum error for the hexane molar fraction is 290.6%. This error corresponds to a simulated molar fraction of 0.0218 and experimental fraction of 0.0056. I.e. the absolute difference between the simulated and experimental molar percentage concentration of hexane in the extract phase is 1.62 percentage points. Similarly, the maximum error for the triethylene glycol molar fraction in the hexane phase is 162.2%. This error corresponds to a simulated triethylene glycol molar fraction of 0.000024 and an experimental molar fraction of 0.000011. Clearly, the large percentage error is misleading in the case of components with very low concentrations in one of the two liquid phases.

It is therefore more meaningful to evaluate the model based on the absolute differences between the simulated and experimental component concentrations in the two liquid phases. All further evaluation of the model proposed for the phenol system as well as those proposed for subsequent liquid-liquid systems will therefore be based on absolute differences between predicted and experimental results, rather than the corresponding percentage errors.

Table 6-3. Average, minimum and maximum absolute differences, δ_{Ave}, δ_{Min}, and δ_{Max} between experimental and simulated molar percentage concentrations of components in the extract and hexane phases for the phenol system.

	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]
Hexane	0.42	0.02	1.62	0.44	0.01	3.20
Water	0.43	0.00	2.46	0.04	0.00	0.38
Mesitylene	0.05	0.00	0.32	0.23	0.00	3.00
5-Et-2-me-pyridine	0.03	0.00	0.20	0.07	0.00	0.53
Aniline	0.04	0.00	0.33	0.02	0.00	0.18
Benzonitrile	0.04	0.00	0.22	0.06	0.00	0.58
Phenol	0.32	0.00	2.94	0.16	0.00	0.98
Triethylene Glycol	0.35	0.00	1.66	0.05	0.00	0.40

Table 6-3 shows that the correlation between the simulated and experimental composition of both the extract and the hexane phase is in fact very good.

It must however be kept in mind that, just as the error percentages between simulated and predicted results can lead to a misleadingly unfavourable evaluation of the proposed model, so the absolute differences can lead to a misleadingly favourable evaluation. As the concentrations of the nitrogen bases, aniline, benzonitrile and 5-et-2-

me-pyridine, are very small in comparison to those of hexane and triethylene glycol, relatively large errors in the distribution of these components between the two phases will still yield very low absolute differences in the molar concentrations of these components in the both the solvent and hexane phases.

Also, the performance of the proposed solvent system is not explicitly evaluated on the basis of composition of the two liquid phases, but on the percentage recovery of the phenolic compounds and either the separation factors obtained between phenol and the other feed components, or the percentage recovery of the nitrogen bases and neutral oils. As such, the correlation between the simulated and experimental values of these parameters should be investigated. As has been discussed previously, the value of the separation factor is extremely sensitive to small fluctuations in phenolic recovery. It is therefore preferable to evaluate the validity of the simulated results on the basis of the recoveries of the neutral oils and nitrogen bases in the extract phase.

In the case of component recoveries, an evaluation of the proposed model based on the absolute differences between the experimental and simulated results is meaningful.

The simulated and experimental recoveries of each of the feed components are shown in Figures 6.6-1 to 6.6-5. The recoveries are plotted in the chronological order in which the experiments were performed.

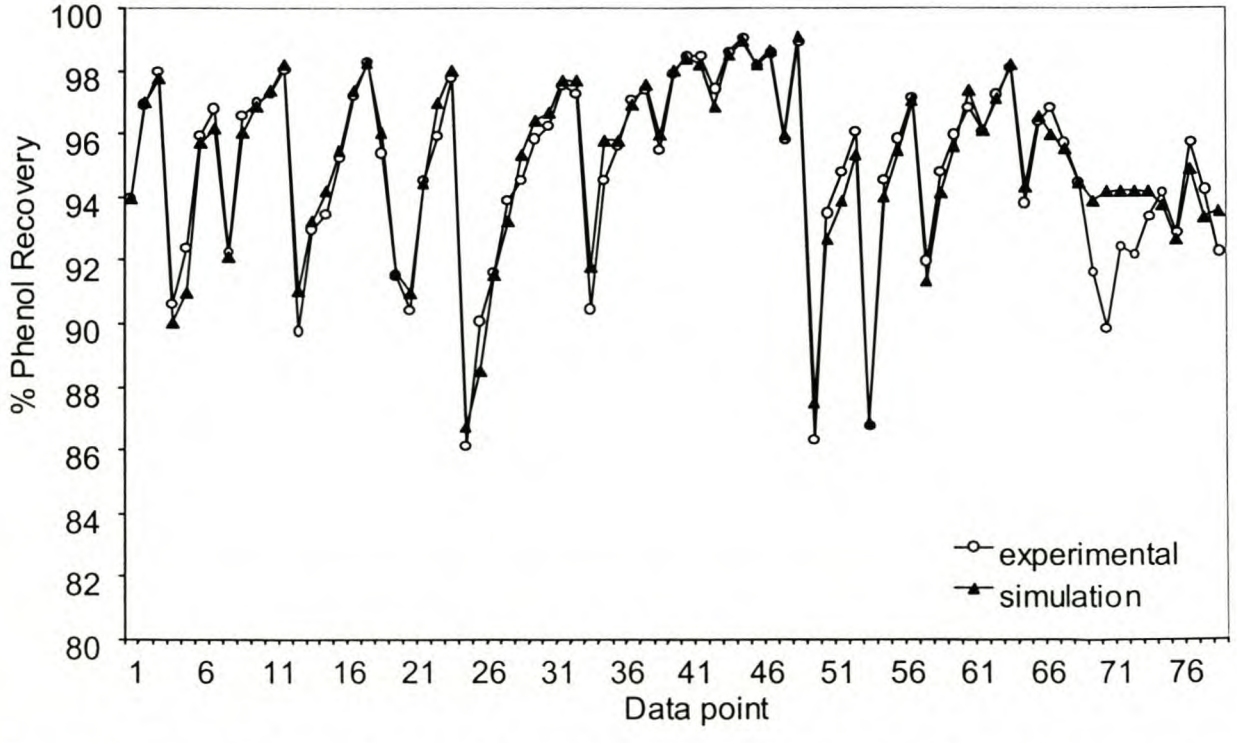


Figure 6.6-1. Comparison of experimental and simulated mass percentage recoveries of phenol in the solvent phase.

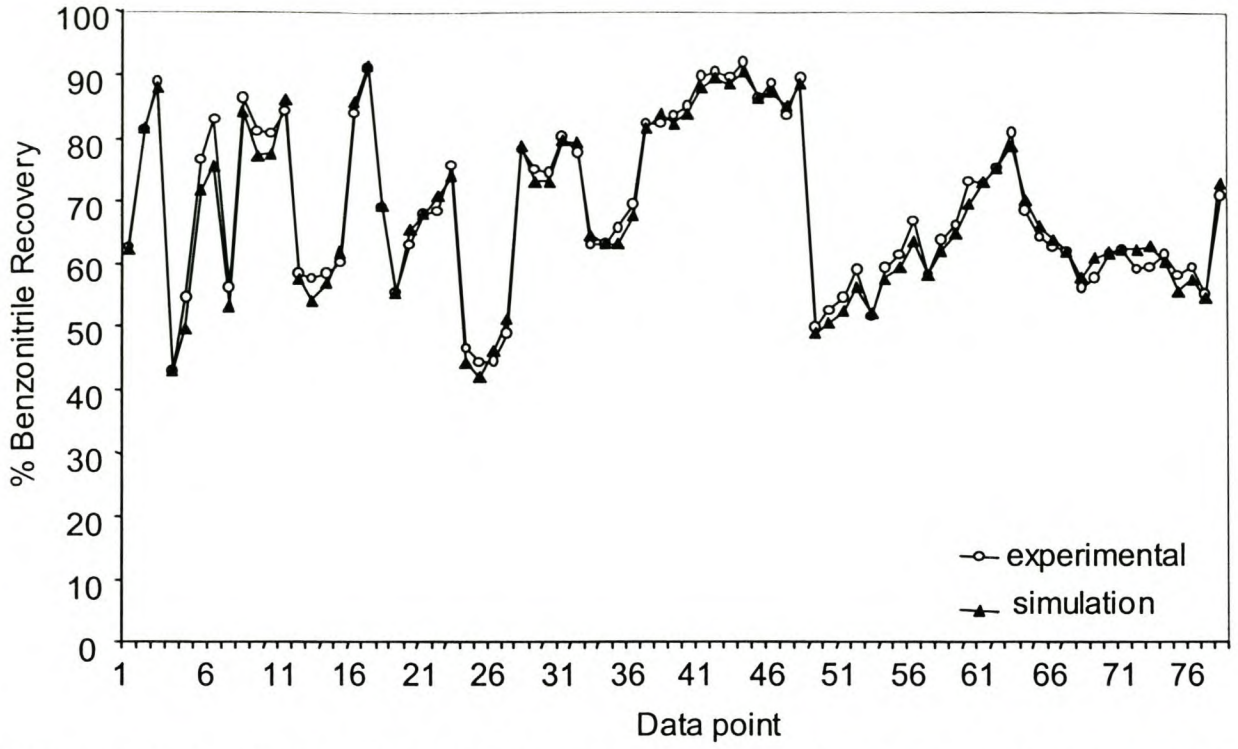


Figure 6.6-2. Comparison of experimental and simulated mass percentage recoveries of benzonitrile in the solvent phase.

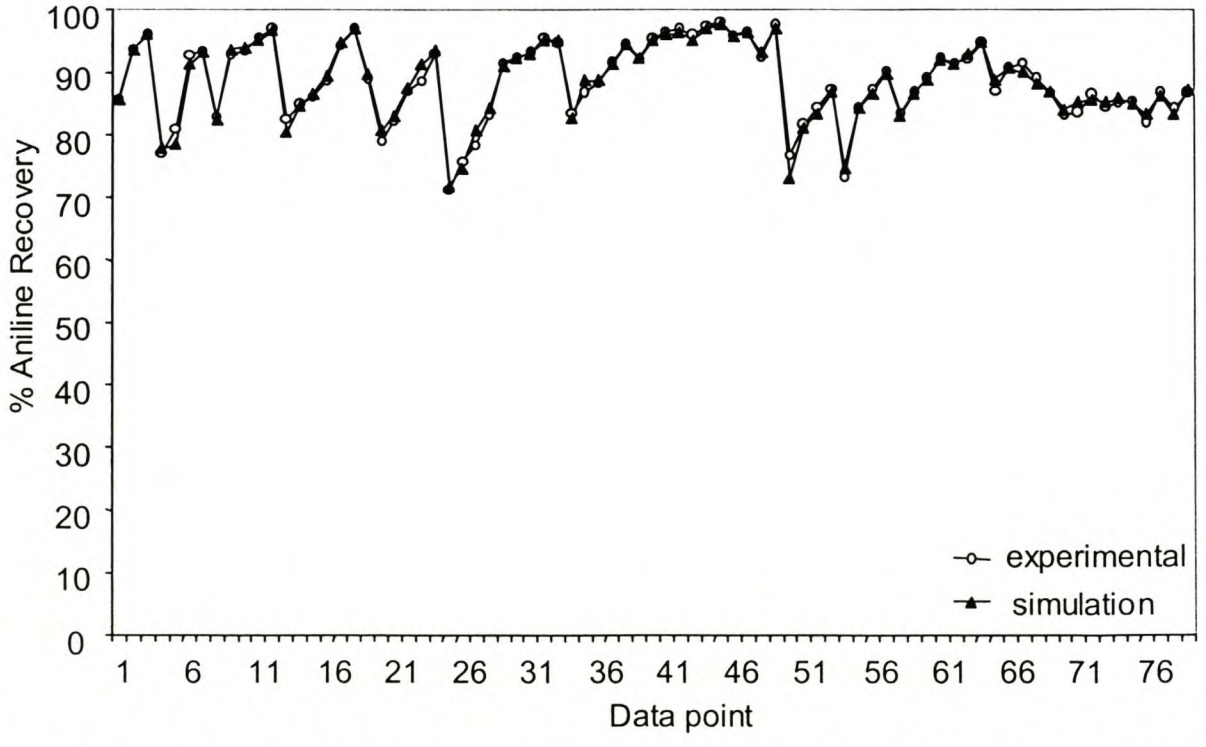


Figure 6.6-3. Comparison of experimental and simulated mass percentage recoveries of aniline in the solvent phase.

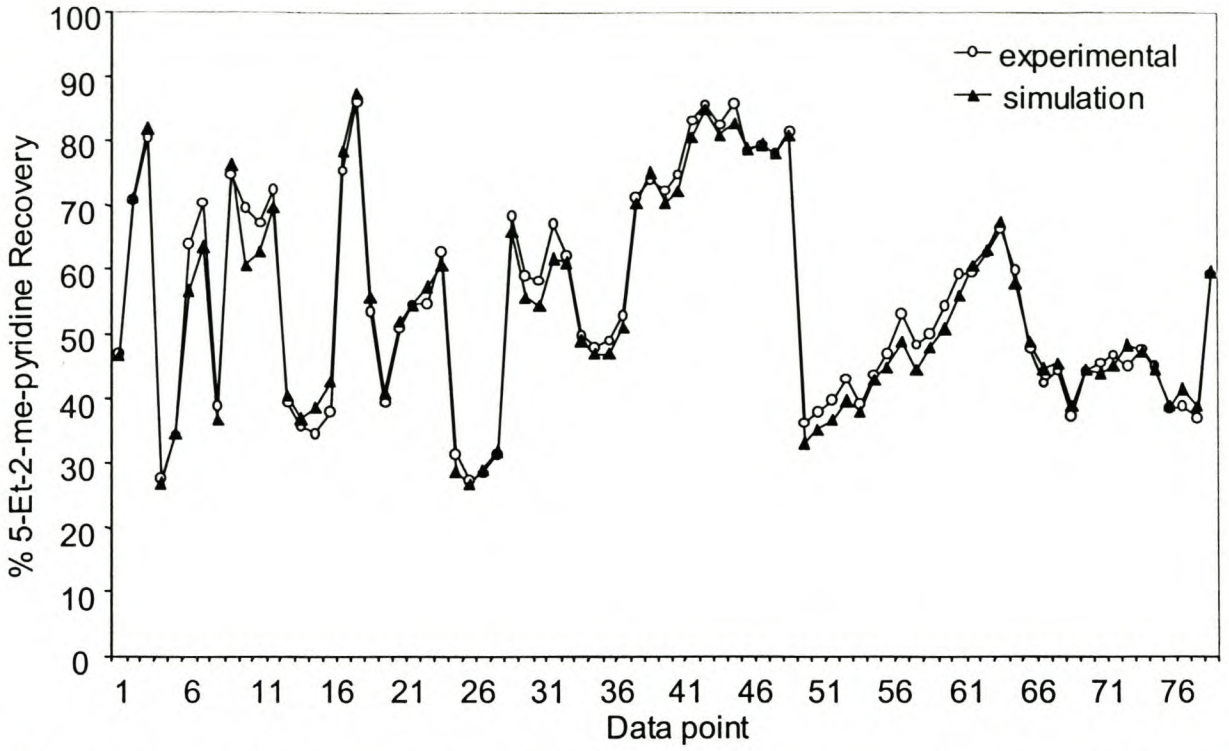


Figure 6.6-4. Comparison of experimental and simulated mass percentage recoveries of 5-et-2-me-pyridine in the solvent phase.

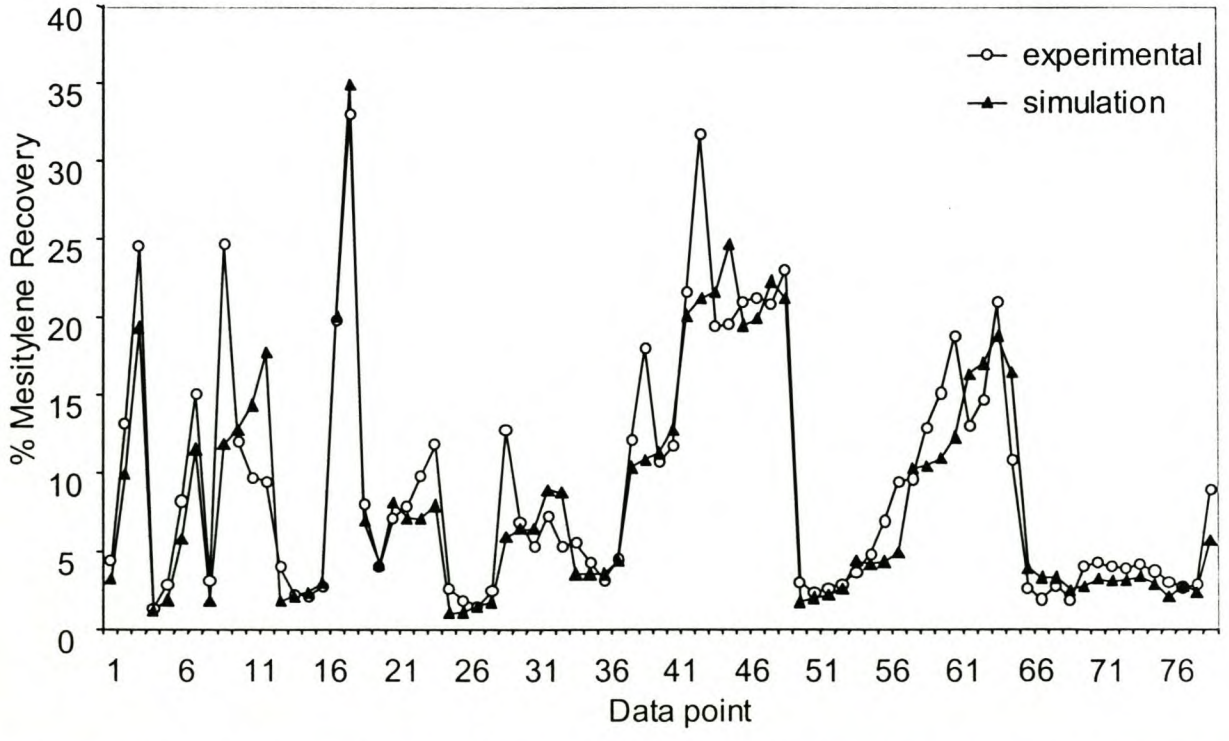


Figure 6.6-5. Comparison of experimental and simulated mass percentage recoveries of Mesitylene in the solvent phase.

Table 6-4. Average, minimum and maximum absolute differences, δ_{Ave}, δ_{Min}, and δ_{Max}, between experimental and simulated percentage recoveries of components in the phenol system.

Component	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]
Hexane	1.06	0.00	8.1
Water	0.06	0.00	0.5
Mesitylene	2.10	0.00	12.9
5-Et-2-me-pyridine	2.00	0.00	8.9
Aniline	0.70	0.00	3.3
Benzonitrile	1.70	0.00	7.3
Phenol	0.60	0.00	4.3
Triethylene Glycol	0.20	0.00	1.4

As can be seen from Table 6-4 and Figure 6.6-1 to Figure 6.6-5, the correlation between the simulated and experimental recoveries for the feed components phenol, benzonitrile, aniline and 5-et-2-me-pyridine as well as triethylene glycol, water and hexane are excellent for most data points.

The maximum absolute differences between the simulated and experimental recoveries of hexane, mesitylene, 5-et-2-me-pyridine and benzonitrile are however significant. These large deviations are all, without exception, applicable to data points that were generated using a hexane to feed ratio of 0.5. This hexane to feed ratio is far removed from the optimum hexane to feed ratio of 5.0 determined for the batch extractions. It is therefore highly unlikely that a hexane to feed ratio as low as 0.5 will be favourable for multistage extractions. As such, the model will not be used for predictions under these circumstances, and its performance in the applicable solvent region is therefore not critical.

A further important consideration in the optimisation of the separation process is the accuracy with which the simulated effect of a change in a parameter, such as the solvent to feed ratio, reflects the effect that would be obtained experimentally.

An indication of the correlation between the simulated and experimental effect of a change in the water to solvent, solvent to feed and hexane to feed ratio can be obtained from Figures 6.6-1 to 6.6-5. The original batch extraction were carried out in sets of four or five extractions. Typically, each set was carried out holding two of the parameters, hexane to feed, solvent to feed or water to solvent ratio, constant and varying the third. So, for example, the solvent to feed ratio was increased in successive batch extractions from 0.5 to 3.0 for the set of batch extractions P15A to P15D. This set of extractions corresponds to the data points 58-61 in Figures 6.6-1 to 6.6-5. The subsequent increase in the recovery of phenol, the nitrogen bases and mesitylene can clearly be seen, as can the fact that the predicted results follow the experimental trend for the data

points in question. It can further be seen in Figures 6.6-1 to 6.6-5 that the predicted results exhibit the same trends as the experimental results, without exception, for phenol and the nitrogen bases. The correlation between the experimental and predicted trends for mesitylene are not as good. This can be expected as the emphasis during regression was placed on the accuracy of the prediction of phenol and nitrogen base distribution between the phases.

The binary parameter set listed in Table 6-1 was therefore accepted for use in further simulations.

6.6.2 m-Cresol System

The optimum binary parameters determined for the m-cresol system, i.e. the nine component liquid-liquid system hexane + water + pseudocumene + undecane + indene + o-tolunitrile + o-toluidine + m-cresol + triethylene glycol, are shown in Table 6-5. These binary parameters were obtained through regression of the 102 LLE data points obtained from the batch extractions executed on the m-cresol feed stream. The weights for the component error terms in the regression goal functions were as follows: hexane, 0.05; water, 0.05; pseudocumene, 0.005; indene, 0.5, o-toluidine, 1.0; o-tolunitrile, 1.0, m-cresol, 1.0 and triethylene glycol, 0.05.

The batch extractions executed on the m-cresol feed stream were simulated using the parameters listed in Table 6-5. The simulated and corresponding experimental molar compositions of the resulting phases are listed in Appendix C2.

Table 6-5. Optimum NRTL binary parameters for the system Hexane(1) + Water(2) + Pseudocumene(3) + Undecane(4) + Indene(5) + o-Tolunitrile(6) + o-Toluidine(7) + + m-Cresol(8) + Triethylene glycol(9). $\alpha_{ij} = \alpha_{ji} = 0.2$.

i	j	b_{ij}	b_{ji}	i	j	b_{ij}	b_{ji}	i	j	b_{ij}	b_{ji}
*1	*2	*1883.50	*3579.90	2	7	884.57	4488.94	4	8	340.62	4720.85
1	3	-437.90	1147.24	2	8	819.63	270.04	4	9	4254.79	-1580.61
1	4	-2141.75	5842.71	*2	*9	* -248.00	*6668.60	5	6	572.44	-402.76
1	5	253.27	-375.26	3	4	4392.00	-1842.83	5	7	283.68	-297.57
1	6	-83.02	2566.88	3	5	876.64	-1976.36	5	8	3276.01	-598.45
1	7	51.95	622.62	3	6	-71.69	3764.98	5	9	487.42	-409.63
1	8	2163.74	-568.34	3	7	15.29	-1003.18	6	7	-1950.24	-372.27
*1	*9	*2164.50	*1559.00	3	8	1871.94	152.37	6	8	572.15	-897.22
2	3	4457.22	4746.21	3	9	5835.40	472.06	6	9	2886.06	-366.29
2	4	1842.81	3365.84	4	5	-1057.01	4502.56	7	8	38.47	-788.81
2	5	4043.78	636.41	4	6	-780.20	6189.99	7	9	1265.30	-969.67
2	6	1070.77	538.48	4	7	-324.53	-440.49	8	9	4578.41	-597.35

*Fixed parameters obtained from regression of phenol system

The absolute differences between the simulated and experimental molar fractions of each component in the extract and hexane phase are listed in Table 6-6.

Table 6-6. Average, minimum and maximum absolute differences, δ_{Ave}, δ_{Min}, and δ_{Max}, between experimental and simulated molar fractions of components in the extract and hexane phases for the m-cresol system.

	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]
Component	Extract Phase			Hexane Phase		
Hexane	1.63	0.00	12.58	0.65	0.00	9.16
Water	0.69	0.00	5.04	0.04	0.00	0.42
Pseudocumene	0.03	0.00	0.28	0.12	0.00	3.15
Undecane	0.01	0.00	0.15	0.13	0.00	3.15
Indene	0.13	0.00	0.93	0.27	0.00	2.84
o-Tolunitrile	0.04	0.00	0.35	0.04	0.00	0.39
o-Toluidine	0.04	0.00	0.42	0.03	0.00	0.29
m-Cresol	0.50	0.00	6.68	0.15	0.00	1.12
Triethylene Glycol	0.90	0.01	6.53	0.07	0.00	0.96

Based on the average absolute differences between experimental and predicted component molar fractions, it can be concluded that the compositions of the hexane and extract phase can be accurately predicted using the proposed model. As with the phenol system, it is necessary to investigate the correlation between the simulated and experimental recovery of each component. This is illustrated in Figures 6.6-6 to 6.6-11.

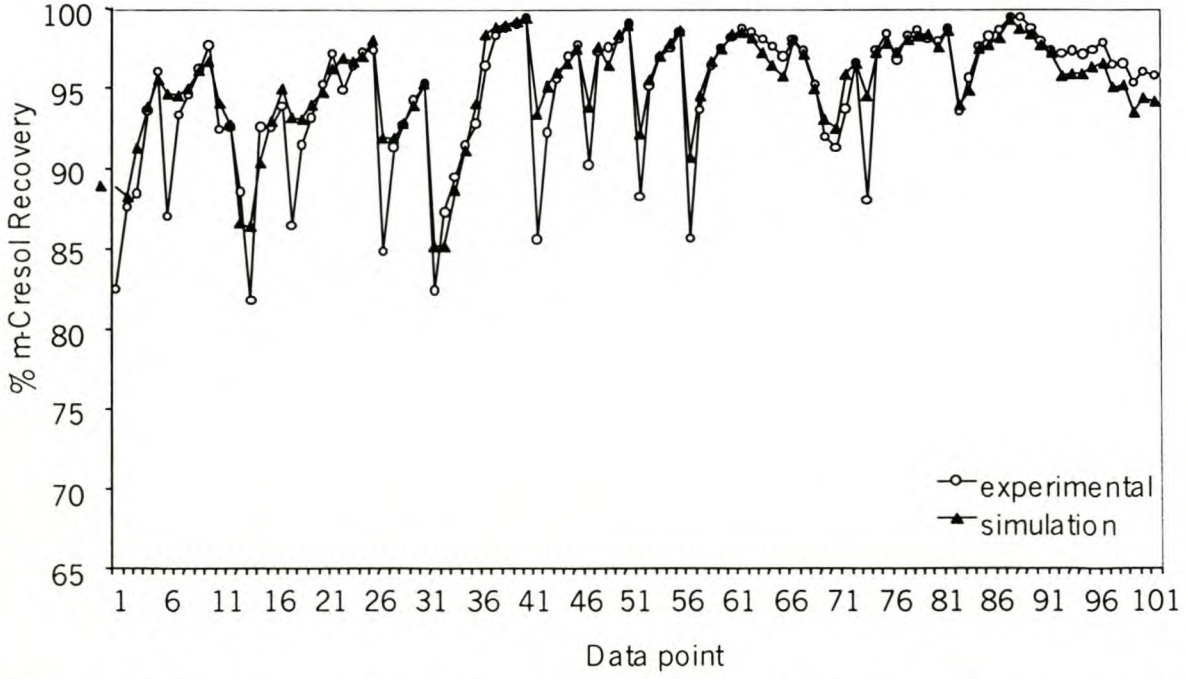


Figure 6.6-6. Comparison of experimental and simulated mass percentage recoveries of m-Cresol in the solvent phase.

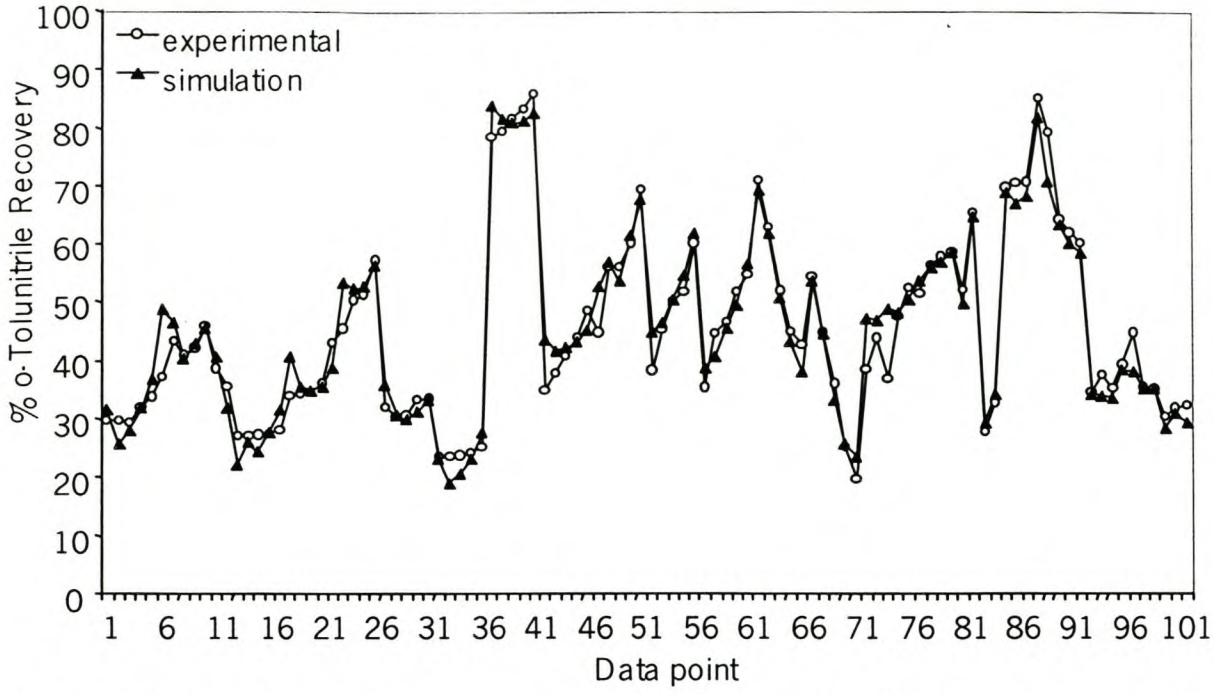


Figure 6.6-7. Comparison of experimental and simulated mass percentage recoveries of o-tolunitrile in the solvent phase.

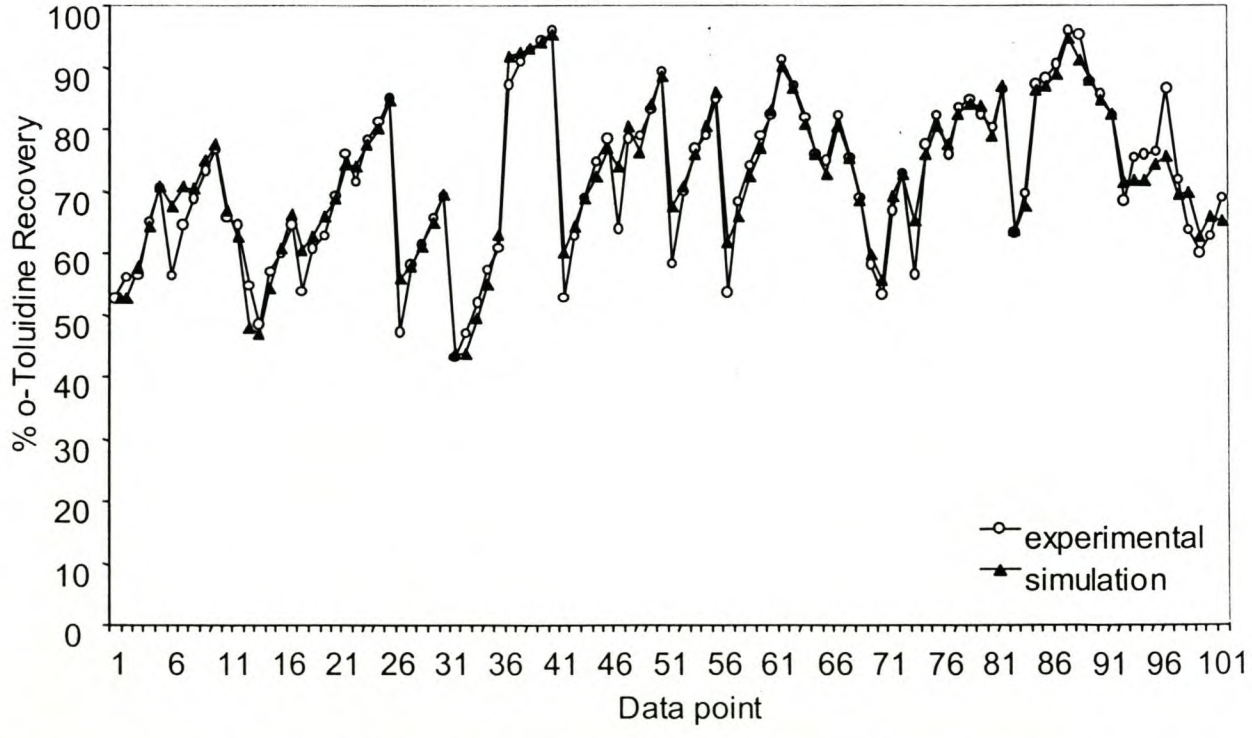


Figure 6.6-8. Comparison of experimental and simulated mass percentage recoveries of o-Toluidine in the solvent phase.

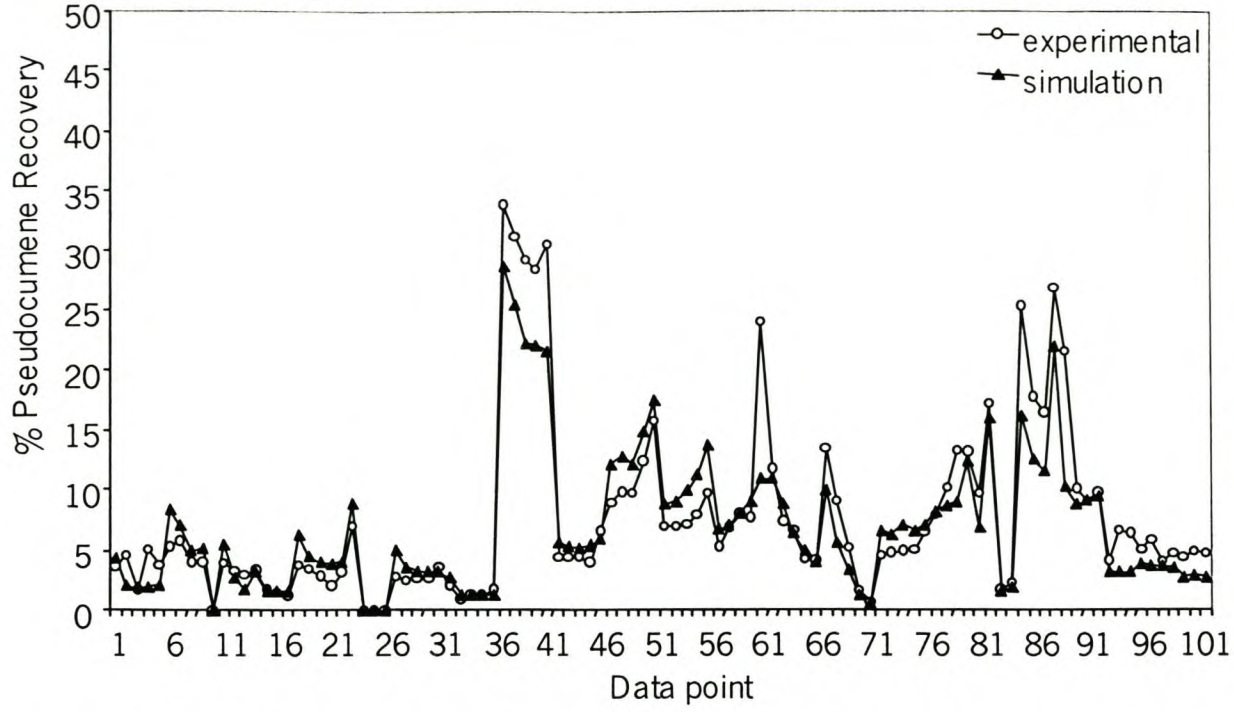


Figure 6.6-9. Comparison of experimental and simulated mass percentage recoveries of pseudocumene in the solvent phase.

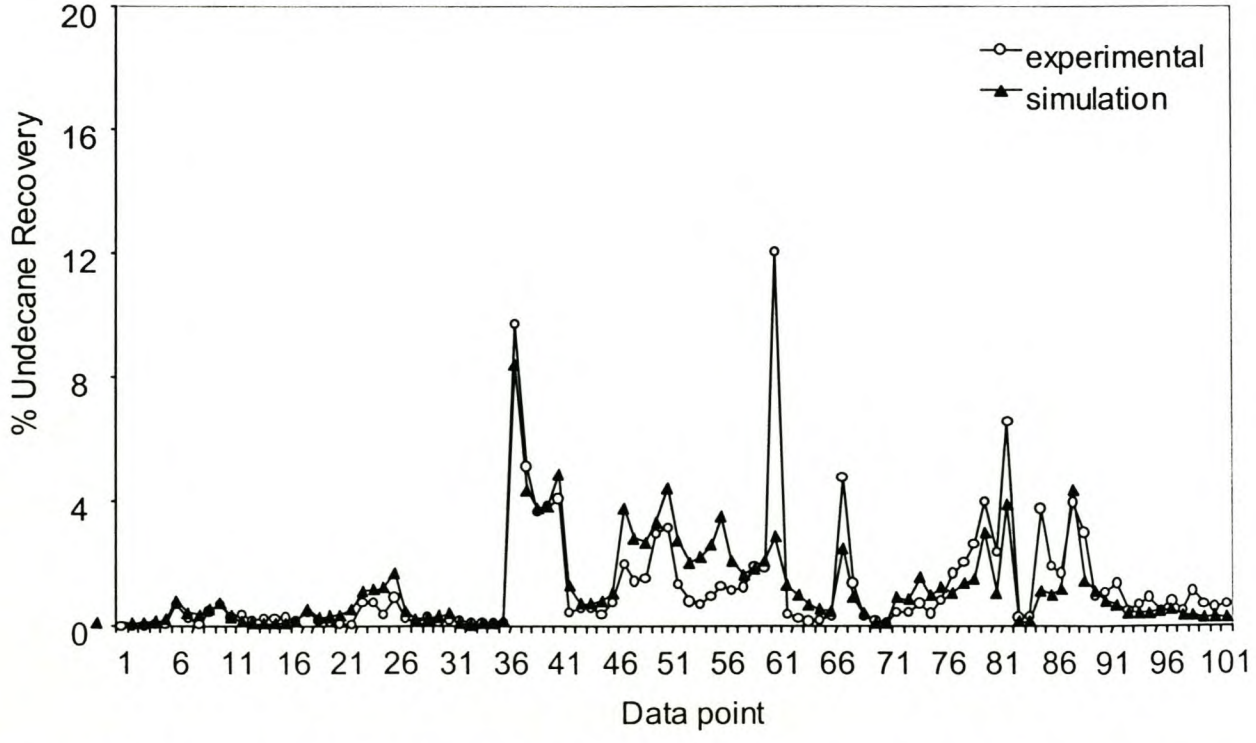


Figure 6.6-10. Comparison of experimental and simulated mass percentage recoveries of undecane in the solvent phase.

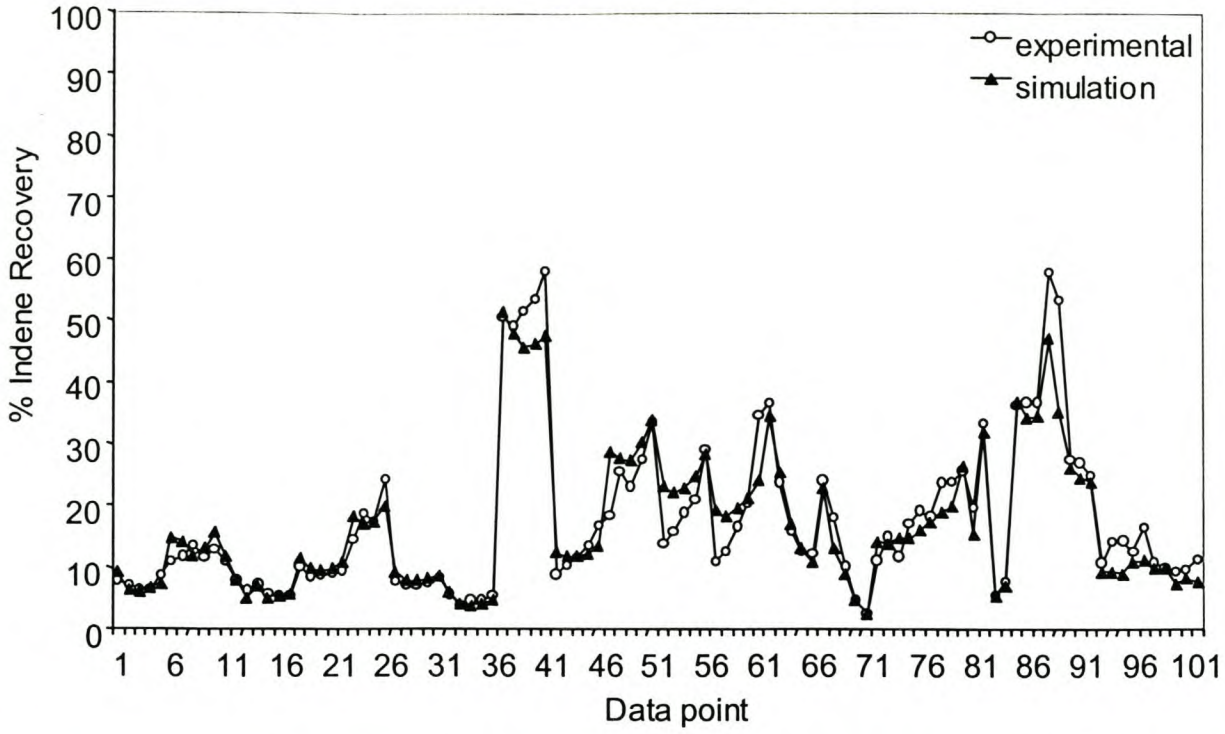


Figure 6.6-11 Comparison of experimental and simulated mass percentage recoveries of indene in the solvent phase.

Table 6-7. Absolute differences in experimental and simulated percentage recoveries of components in m-cresol system.

Components	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]
Hexane	1.7	0.0	29.9
Water	0.1	0.0	0.5
Pseudocumene	2.0	0.0	13.0
Undecane	0.6	0.0	9.2
Indene	2.6	0.0	18.1
o-Tolunitrile	2.4	0.0	11.8
o-Toluidine	2.3	0.0	11.4
m-Cresol	1.3	0.0	7.9
Triethylene Glycol	2.6	0.0	18.3

As can be seen from Figure 6.6-6 to Figure 6.6-11, the correlation between the simulated and experimental m-cresol, o-tolunitrile and o-toluidine recoveries is very good. A good correlation between simulated and experimental indene and pseudocumene recoveries is also obtained. While a noticeable correlation can be observed between the simulated and experimental undecane recoveries shown in

Figure 6.6-10 it appears that these recoveries are not predicted with the same level of accuracy as the other feed components. This is due to the extremely low solubility of undecane in the solvent phase, and consequently, the very low recovery values. The absolute differences between the predicted and experimental undecane recoveries, which are given in Table 6-7, are in fact very small.

The values of the absolute differences between the simulated and experimental component recoveries listed in Table 6-7 confirm that the proposed model can accurately predict not only the recoveries of the feed components, but also those of hexane, water and triethylene glycol.

A very good correlation is obtained between the trends exhibited by the simulated and experimental results for m-cresol, o-tolunitrile and o-toluidine especially.

As was found in modelling the phenol system, single large deviations of the simulated results from the experimental results occur at single data points, which, with one exception, correspond to batch extractions executed using a low hexane to feed ratio of 0.5. The largest deviations applicable to undecane and pseudocumene recoveries occur at a data point generated using a water to solvent ratio of 0.0, solvent to feed ratio of 3.0 and hexane to feed ratio of 5.0. The recoveries of the other components in the system are accurately predicted for this data point. As the separation of m-cresol from undecane and pseudocumene is trivial, the inaccurate prediction of the recovery of these two neutral oils for these solvent ratios is not considered to be critical.

As has been noted, the accurate prediction of m-cresol and nitrogen base recoveries is most critical in evaluating the performance of the proposed solvent system. The proposed model predicts the m-cresol, o-tolunitrile and o-toluidine recoveries, as well as the trends exhibited in these recoveries, very well. While the accuracy of the predictions of undecane and pseudocumene are not as good, it is satisfactory. Also, pseudocumene and undecane are not present in significant quantities in the feed stream used for the pilot plant tests. Any error in the determination of the binary parameters applicable to these two components will therefore not be propagated in the regression of subsequent liquid-liquid systems. The binary parameter set listed in Table 6-7 was therefore considered satisfactory and accepted as a basis for the modelling of the multicomponent system applicable to the pilot plant tests.

6.6.2.1 m-, p-Cresol System

The m-, p-cresol system is the multicomponent LLE system generated with a series of 22 batch extractions using a feed stream consisting of o-tolunitrile, m-cresol and p-cresol. The components present in the m-, p-cresol system are therefore hexane,

water, o-tolunitrile, m-cresol, p-cresol and triethylene glycol. The masses of the components added to the batch extractions and the corresponding masses in the resulting phases are listed in Appendix C3. These additional batch extractions were executed in order to generate data for the determination of binary parameters applicable to p-cresol. The only parameters in the m-,p-cresol system that are not already determined in the regression of the m-cresol system are the 12 binary parameters applicable to the binary component pairs containing p-cresol.

The optimum parameters obtained for the m-, p-cresol system are listed in Table 6-8. The weights accorded to the component error terms in the regression goal function were: hexane, 0.05; water, 0.05; o-tolunitrile, 1.0; m-cresol, 1.0; p-cresol, 1.0 and triethylene glycol, 0.005.

Table 6-8. Optimum NRTL binary parameters for the system Hexane(1) + Water(2) + o-Tolunitrile(3) + m-Cresol(4) + p-Cresol(5) + Triethylene glycol(6). $\alpha_{ij} = \alpha_{ji} = 0.2$.

i	j	b_{ij}		b_{ji}	
1	2	1883.5	**	3579.9	**
1	3	-83.02	*	2566.88	*
1	4	2163.735	*	-568.341	*
1	5	3411.378		-867.235	
1	6	2164.5	**	1559	**
2	3	1070.77	*	538.48	*
2	4	819.63	*	270.035	*
2	5	1290.274		6799.999	
2	6	-248	**	6668.6	**
3	4	572.15	*	-897.221	*
3	5	2283.992		-1082.3	
3	6	2886.056	*	-366.289	*
4	5	1320.74		-857.157	
4	6	4578.407	*	-597.346	*
5	6	3453.312	*	262.396	*

**Fixed parameters obtained by regression of phenol system

*Fixed parameters obtained by regression of m-cresol system

Table 6-9 lists the absolute differences between the experimentally determined molar fractions of the components in both liquid phases and those predicted by means of simulations using the parameters listed in Table 6-8.

Table 6-9. Average, minimum and maximum absolute differences, δ_{Ave}, δ_{Min}, and δ_{Max}, between experimental and simulated molar fractions of components in the extract and hexane phases.

	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]
	Extract Phase			Hexane Phase		
Hexane	1.0	0.0	3.7	0.2	0.0	1.0
Water	0.9	0.0	3.3	0.0	0.0	0.1
o-Tolunitrile	0.0	0.0	0.1	0.1	0.0	0.3
m-cresol	0.2	0.0	0.4	0.1	0.0	0.3
p-Cresol	0.2	0.0	0.4	0.1	0.0	0.3
Triethylene Glycol	0.5	0.0	1.1	0.0	0.0	0.3

Based on the average absolute differences between experimental and predicted component molar fractions, it can be concluded that the compositions of the hexane and extract phase can be accurately predicted using the proposed model. As with the phenol and m-cresol systems, the correlation between the simulated and experimental recoveries of each feed component must be investigated. This is illustrated in Figures 1.6-12 to 1.6-14. The absolute differences in experimental and predicted mass recoveries of each component in the system are listed in Table 6-10.

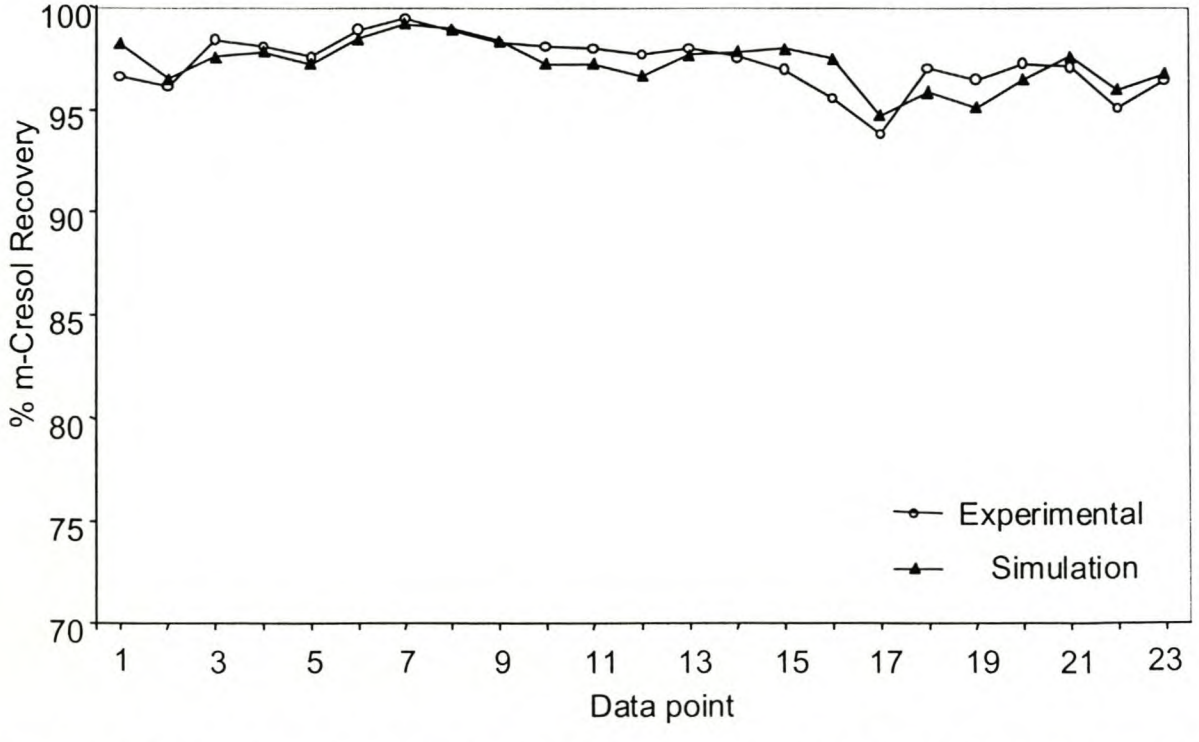


Figure 6.6-12. Comparison of experimental and simulated mass percentage recoveries of m-cresol in the solvent phase.

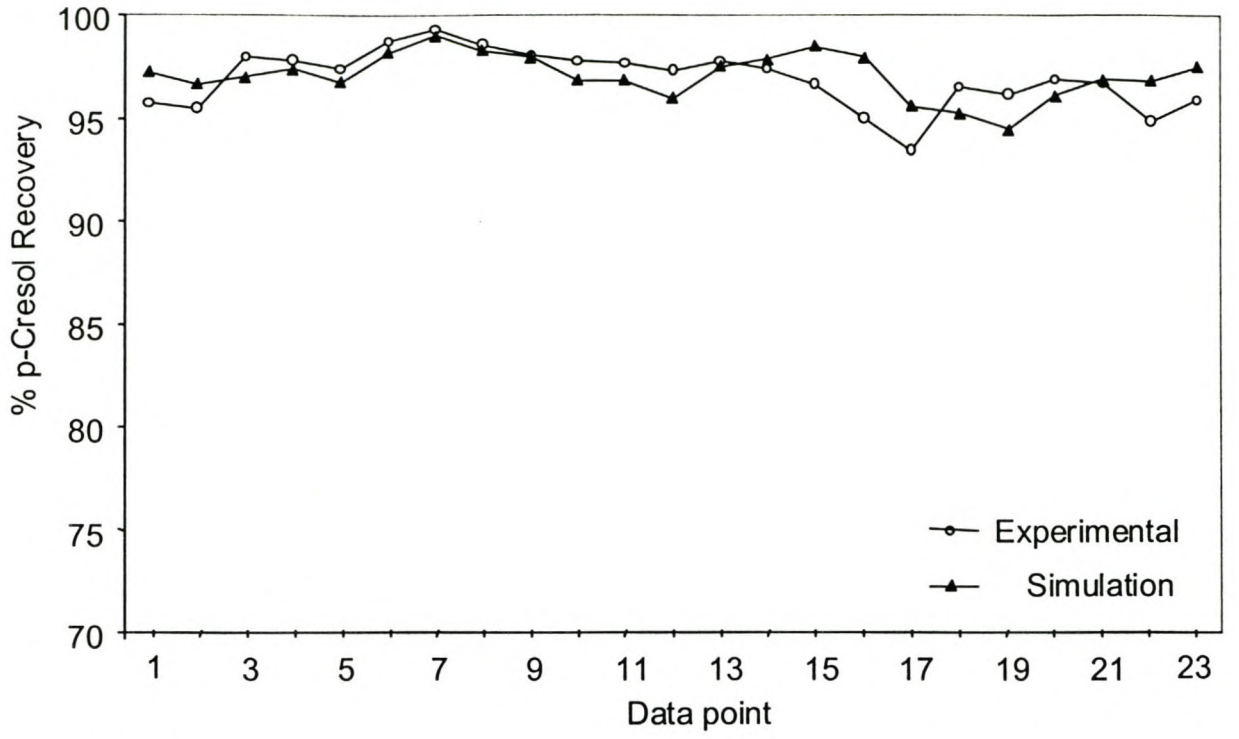


Figure 6.6-13. Comparison of experimental and simulated mass percentage recoveries of p-cresol in the solvent phase.

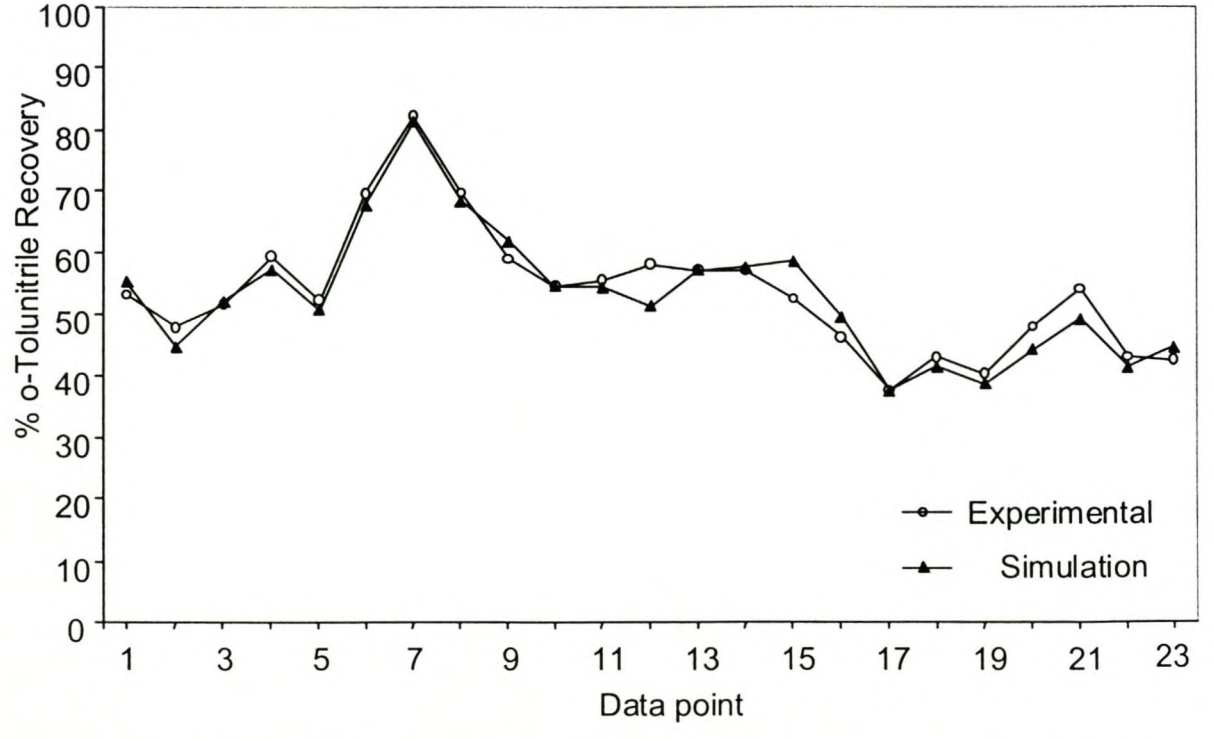


Figure 6.6-14. Comparison of experimental and simulated mass percentage recoveries of o-tolunitrile in the solvent phase.

Table 6-10. Absolute differences in experimental and simulated percentage recoveries of components in m-, p-cresol system.

Components	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]
Hexane	1.4	0.0	5.9
Water	0.0	0.0	0.2
o-Tolunitrile	2.2	0.0	6.8
m-Cresol	0.7	0.1	2.0
p-Cresol	1.0	0.2	2.9
Triethylene Glycol	0.0	0.0	0.1

It can be seen from Figures 6.6-12 to 6.6-14 and Table 6-10 that the correlation obtained between the predicted and experimental component recoveries is very good. While it initially appears as if there are significant discrepancies in the prediction m-cresol and, especially p-cresol for some data points, if can be seen from Table 6-10 that the maximum discrepancies between predicted and experimental m-cresol and p-cresol recoveries are only 2.0 and 2.9 percentage points respectively. With the exception of a single data point, the recovery of o-tolunitrile is extremely accurately predicted. The same is true of hexane. It can also be seen from Table 6-10 that the model predicts the distribution of water and triethylene glycol between the two phases extremely accurately.

It is important to note that the binary parameters determined in the absence of p-cresol can successfully be applied to a system containing p-cresol. While this is not conclusive proof that these parameters are in fact the optimum parameters for the component pairs in question, it does indicate that the regression algorithm used in their determination is not susceptible to local minima traps.

The binary parameters obtained for the m-, p-cresol system can therefore be used as a basis for the modelling of other systems.

6.6.2.2 Aniline - Cresol System

The aniline - cresol system is the seven component LLE system generated with a series of 12 batch extractions using a feed stream consisting of aniline, o-tolunitrile, m-cresol and p-cresol. I.e. the aniline – cresol system is the system hexane + water + aniline + o-tolunitrile + m-cresol + p-cresol + triethylene glycol. The masses of the components added to the batch extractions and the corresponding masses in the resulting phases are listed in Appendix C4. This series of batch extractions was carried out in order to generate data for the determination of binary parameters for the component pairs aniline + o-tolunitrile, aniline + m-cresol and aniline + p-cresol. The binary parameters

for the component pairs aniline + hexane, aniline + water and aniline + triethylene glycol were previously determined for the phenol system, while the binary parameters applicable p-cresol are those determined for the m-,p-cresol system. The binary parameters for the component pairs m-cresol + hexane, m-cresol + water, m-cresol + o-tolunitrile, m-cresol + triethylene glycol, o-tolunitrile + triethylene glycol, o-tolunitrile + water and o-tolunitrile + hexane were determined for the m-cresol system. Therefore, of the 42 binary parameters required to model the aniline-cresol system, only 6 have yet to be determined.

The optimum parameters obtained through regression for the aniline-cresol system are listed in Table 6-11. The weights of the component error terms in the goal function of the regression algorithm were specified as follows: hexane, 0.05; water, 0.05; aniline, 1.0; o-tolunitrile, 1.0; m-cresol, 1.0; p-cresol, 1.0 and triethylene glycol, 0.005.
lists the absolute differences between the experimentally determined molar fractions of the components in both liquid phases and those predicted by means of simulations using the parameters listed in Table 6-11.

Table 6-11. Optimum NRTL binary parameters for the system Hexane(1) + Water(2) + Aniline(3) + o-Tolunitrile(4) + m-Cresol(5) + p-Cresol(6) + Triethylene glycol(7). $\alpha_{ij} = \alpha_{ji} = 0.2$.

i	j	b_{ij}	b_{ji}	i	j	b_{ij}	b_{ji}
1	2	1883.50 **	3579.90 **	3	4	3208.00	4904.00
1	3	481.50 **	503.20 **	3	5	-616.94	1403.00
1	4	-83.02 *	2566.88 *	3	6	145.27	-100.00
1	5	2163.74 *	-568.34 *	3	7	278.60 **	-450.30 **
1	6	3411.38 #	-867.24 #	4	5	572.15 *	-897.22 *
1	7	2164.50 **	1559.00 **	4	6	2283.99 #	-1082.30 #
2	3	950.40 **	62.63 **	4	7	2886.06 *	-366.29 *
2	4	1070.77 *	538.48 *	5	6	1320.74 #	-857.16 #
2	5	819.63 *	270.04 *	5	7	4578.41 *	-597.35 *
2	6	1290.27 #	6800.00 #	6	7	3453.31 #	262.40 #
2	7	-248.00 **	6668.60 **				

**Fixed parameters obtained by regression of phenol system
*Fixed parameters obtained by regression of m-cresol system
#Fixed parameters obtained by regression of m-, p-cresol system

Table 6-12. Average, minimum and maximum absolute differences, δ_{Ave}, δ_{Min}, and δ_{Max}, between experimental and simulated molar fractions of components in the extract and hexane phases for the aniline-cresol system.

	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]
	Extract Phase			Hexane Phase		
Hexane	3.42	0.15	13.04	0.40	0.05	0.91
Water	1.74	0.09	5.29	0.02	0.00	0.04
Aniline	0.05	0.00	0.28	0.04	0.01	0.08
o-Tolunitrile	0.03	0.00	0.07	0.03	0.00	0.10
m-cresol	0.32	0.01	1.86	0.08	0.00	0.27
p-Cresol	0.24	0.01	1.58	0.15	0.02	0.42
Triethylene Glycol	1.22	0.11	3.95	0.11	0.00	0.94

Table 6-12 shows that the composition of the hexane phase is accurately predicted with respect to all components in the system. In the solvent phase, however, the prediction of the hexane concentration is significantly less accurate than the predicted concentrations of the other components in this phase. This is especially significant as the concentration of hexane in the solvent phase is very low. I.e. a large absolute difference in the predicted and experimental hexane concentrations indicates that the predicted solubility of hexane in the solvent phase differs significantly from the experimental solubility.

The large average absolute difference between the predicted and experimental hexane concentration in the solvent phase is however due to the large value, 13.0 percentage points, of the maximum absolute difference. This value corresponds to the first data point in the set, as does the maximum absolute difference obtained between the predicted and experimental water concentrations in the solvent phase. As the distribution of water and hexane between the two phases is largely determined by the values of the binary parameters applicable to the component pairs, water-hexane, hexane-triethylene glycol and water-triethylene glycol, and as these binary parameters have proved to yield accurate results for the phenol, m-cresol and m-,p-cresol systems, it is likely that the large discrepancy for the data point in question can be attributed to an error in the experimental determination of the point, rather than an error in the predicted value.

The correlation between the simulated and experimental mass recoveries of aniline, o-tolunitrile, m-cresol and p-cresol are illustrated in Figures1.6-15 to 1.6-18. The absolute differences in experimental and predicted mass recoveries of each component in the system are listed in Table 6-13.

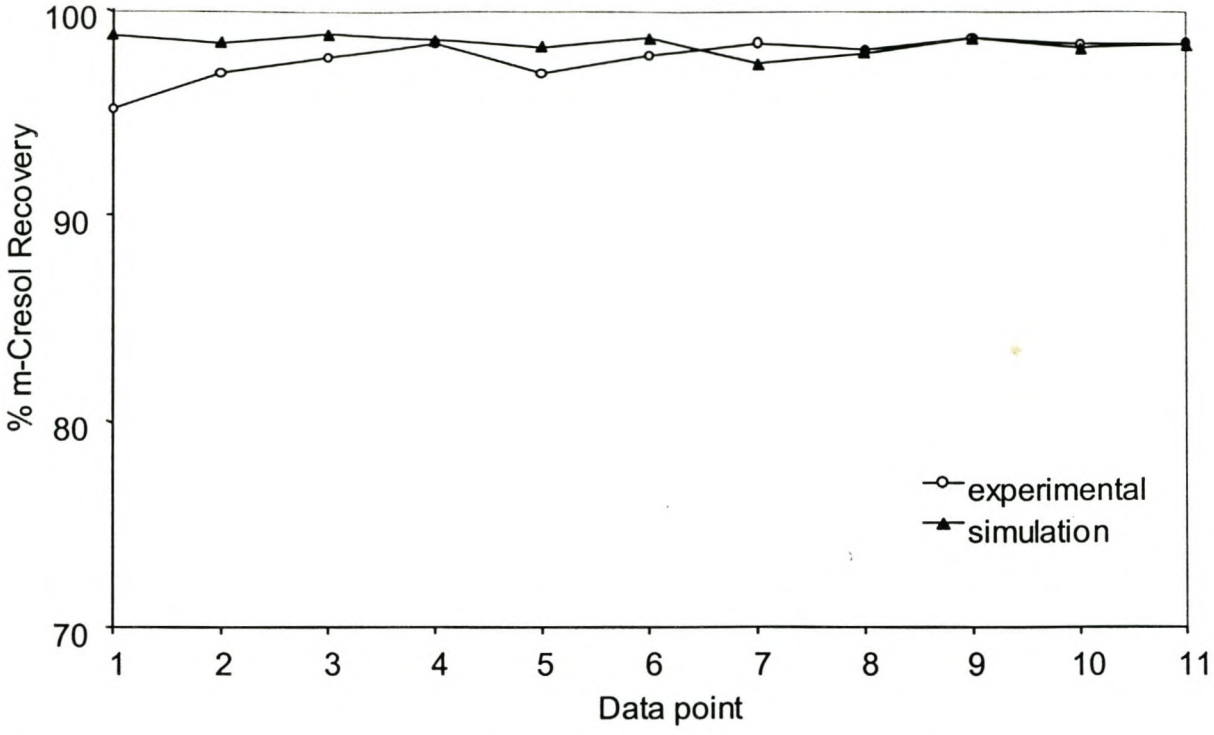


Figure 6.6-15. Comparison of experimental and simulated mass percentage recoveries of m-cresol in the solvent phase.

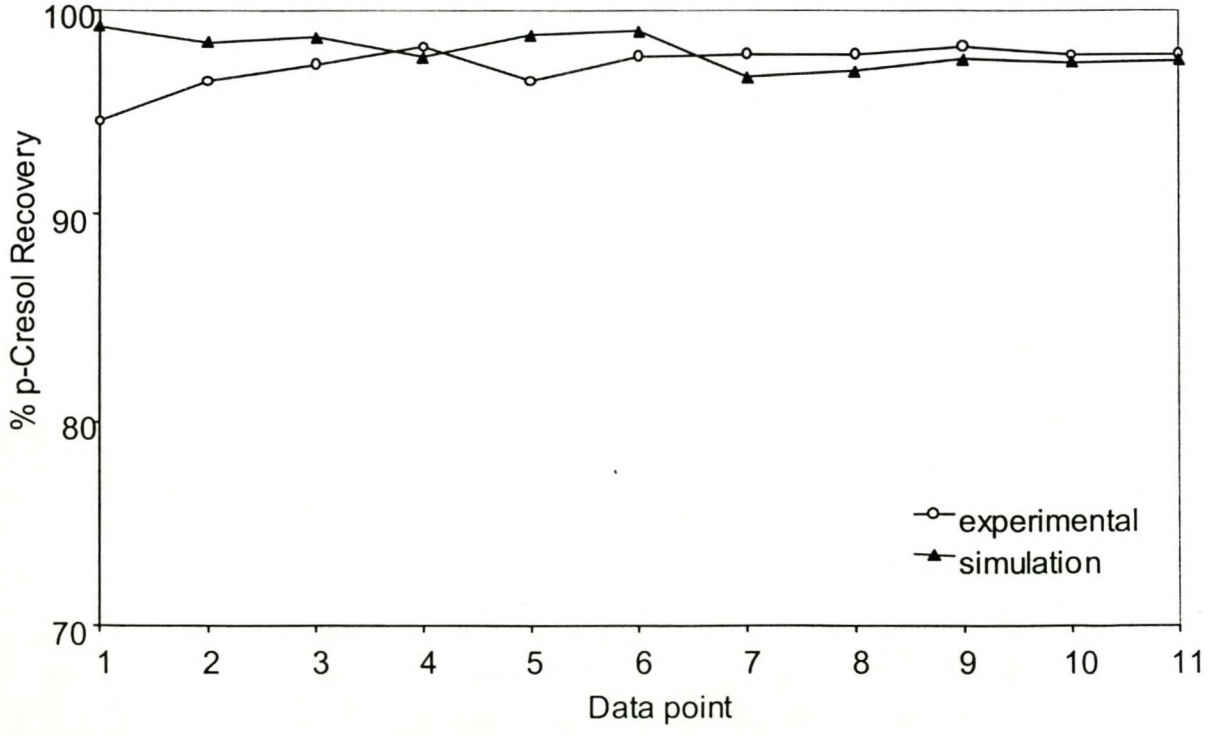


Figure 6.6-16. Comparison of experimental and simulated mass percentage recoveries of p-cresol in the solvent phase.

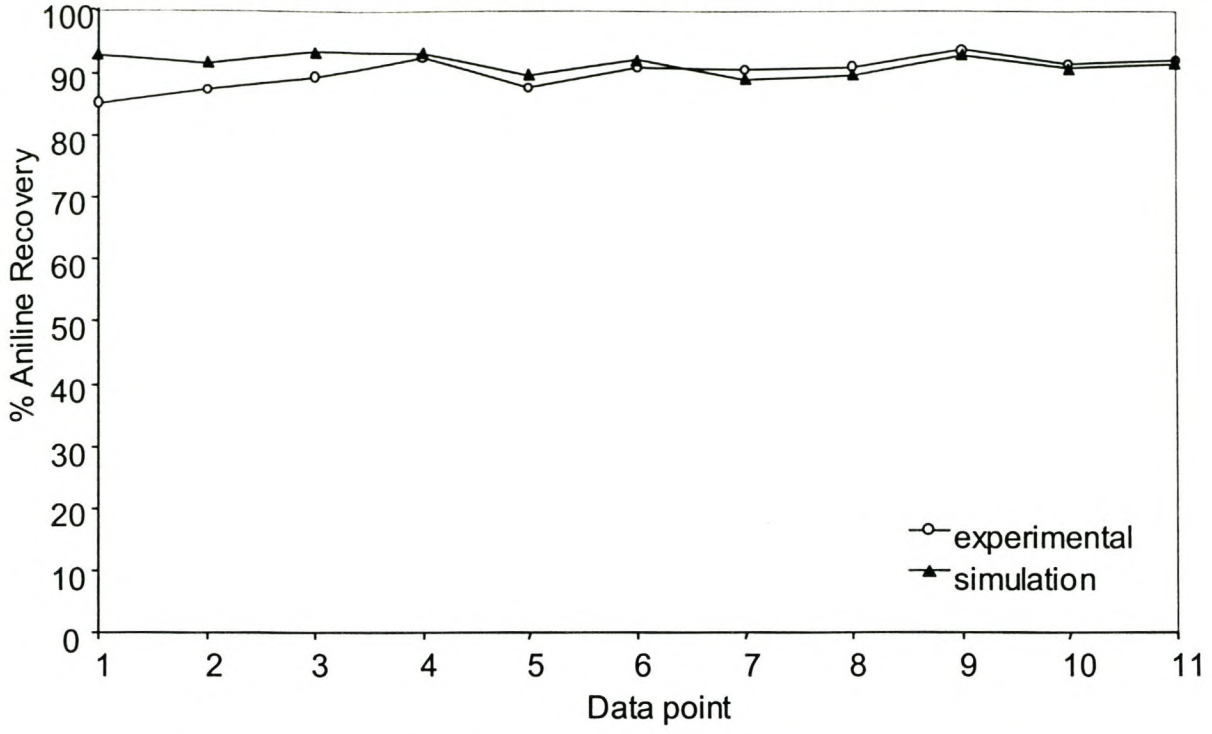


Figure 6.6-17. Comparison of experimental and simulated mass percentage recoveries of aniline in the solvent phase.

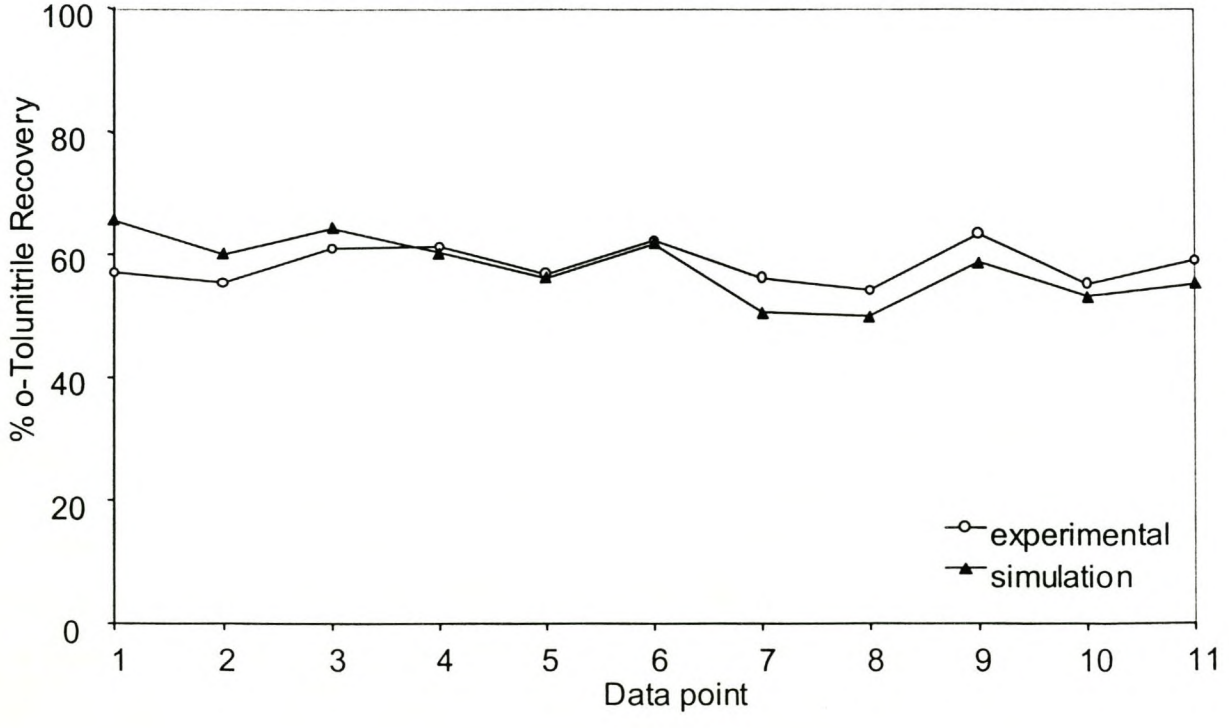


Figure 6.6-18. Comparison of experimental and simulated mass percentage recoveries of o-tolunitrile in the solvent phase.

Table 6-13. Absolute differences in experimental and simulated percentage recoveries of components in m-, p-cresol system.

Components	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]
Hexane	2.8	0.1	8.5
Water	0.04	0.02	0.07
Aniline	2.3	0.7	7.6
o-Tolunitrile	3.6	0.6	8.6
m-Cresol	0.9	0.0	3.6
p-Cresol	1.4	0.3	4.6
Triethylene Glycol	0.4	0.0	2.2

It can be seen from Figures 6.6-15 to 6.6-18 that, apart from the first two data points, a good correlation is obtained between the simulated and experimental values of the feed components. The absolute differences between the simulated and experimental recoveries listed in Table 6-13 confirm this finding. The maximum deviation of predicted from experimental recovery values, for all the components in the system are applicable to the first data point.

Figures 6.6-15 to 6.6-18 show that the predicted and simulated recovery values for all the components exhibit the same trends. It can therefore be concluded that the proposed set of binary parameters can be used with confidence as a basis for further simulations.

It should also be noted that the majority of the binary parameters used in the prediction of the aniline-cresol system were not obtained from the regression of this specific system. 24 of the 42 parameters were obtained by regression of systems containing components not present in the aniline-cresol system and a further 12 were obtained for a system not containing aniline. The underlying assumptions of the NRTL equation can therefore be concluded to be physically meaningful.

6.6.3 Xylenol System

The optimum binary parameters determined for the xylenol system, i.e. the nine-component liquid-liquid system hexane + water + indane + dodecane + naphthalene + 2,4-xylenol + 3,5-xylenol + 3,4-xylenol + triethylene glycol, are shown in Table 6-14. These binary parameters were obtained through regression of the 79 LLE data points

obtained from the batch extractions executed on the xylenol feed stream. The weights for the component error terms in the goal functions were as follows: hexane, 0.05; water, 0.05; indane, 0.5; dodecane, 0.05, naphthalene, 1.0; 2,4-xylenol, 1.0, 3,5-xylenol, 1.0, 3,4-xylenol, 1.0 and triethylene glycol, 0.05.

The batch extractions executed on the xylenol feed stream were simulated using the parameters listed in Table 6-14. The simulated and corresponding experimental molar compositions of the resulting phases are listed in Appendix C5.

The absolute differences between the simulated and experimental molar fractions of each component in the extract and hexane phase are listed Table 6-15.

Table 6-14. Optimum NRTL binary parameters for the system Hexane (1) + Water (2) + Indane (3) + Dodecane (4) + Naphthalene (5) + 2,4-Xylenol (6) + 3,5-Xylenol (7) + 3,4-Xylenol (8) + Triethylene glycol (9). $\alpha_{ij} = \alpha_{ji} = 0.2$.

i	j	b_{ij}	b_{ji}	i	j	b_{ij}	b_{ji}	i	j	b_{ij}	b_{ji}
*1	*2	*1883.50	*3579.90	2	7	3283.26	2930.22	4	8	5256.00	3294.94
1	3	662.80	7109.68	2	8	3178.45	3969.44	4	9	1382.00	-67.09
1	4	4451.29	-1369.38	*2	*9	*-248.00	*6668.60	5	6	9086.92	7457.86
1	5	231.44	-326.19	3	4	348.86	-601.99	5	7	2556.49	990.98
1	6	2276.17	4526.16	3	5	475.00	2684.98	5	8	1952.95	1169.98
1	7	3852.82	4099.85	3	6	846.48	-856.57	5	9	536.95	-359.80
1	8	2798.49	4831.69	3	7	4356.92	933.42	6	7	2602.12	2082.25
*1	*9	*2164.50	*1559.00	3	8	828.30	598.99	6	8	2100.01	1775.39
2	3	2351.00	4756.21	3	9	-68.27	356.75	6	9	3932.52	334.66
2	4	6977.00	434.00	4	5	119.00	4015.97	7	8	2574.91	2488.55
2	5	3817.02	699.93	4	6	9100.17	540.55	7	9	2850.13	785.22
2	6	2544.85	5852.87	4	7	4963.00	-157.25	8	9	2176.37	876.55

*Fixed parameters obtained from regression of phenol system

Table 6-15. Average, minimum and maximum absolute differences, δ_{Ave}, δ_{Min}, and δ_{Max}, between experimental and simulated molar fractions of components in the extract and hexane phases for the xylenol system.

	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]
	Extract Phase			Hexane Phase		
Hexane	0.84	0.05	4.82	0.56	0.00	4.99
Water	0.63	0.00	2.80	0.06	0.00	0.32
Indane	0.01	0.00	0.09	0.04	0.00	0.20
Dodecane	0.02	0.00	0.09	0.10	0.00	0.77
Naphthalene	0.44	0.00	2.91	0.43	0.00	4.69
2,4-Xylenol	0.21	0.00	1.72	0.08	0.00	1.13
3,5-Xylenol	0.14	0.00	1.08	0.05	0.00	0.28
3,4-Xylenol	0.09	0.00	0.91	0.02	0.00	0.08
Triethylene Glycol	0.53	0.01	4.34	0.29	0.00	1.59

Based on the average absolute differences between experimental and predicted component molar fractions, it can be concluded that the compositions of the hexane and extract phase can be accurately predicted using the proposed model. A comparison between the simulated and experimental recoveries of each feed component are illustrated in Figures 6.6-19 to 1.6-23.

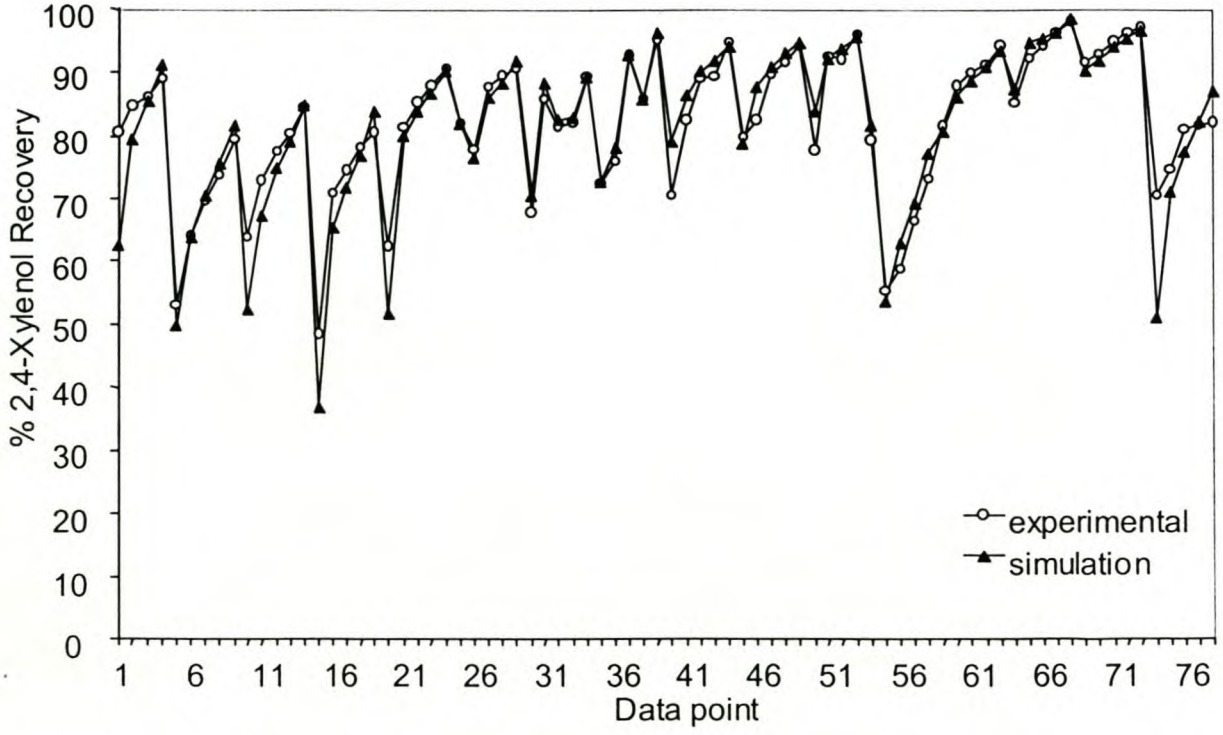


Figure 6.6-19. Comparison of experimental and simulated mass percentage recoveries of 2,4-xylenol in the solvent phase.

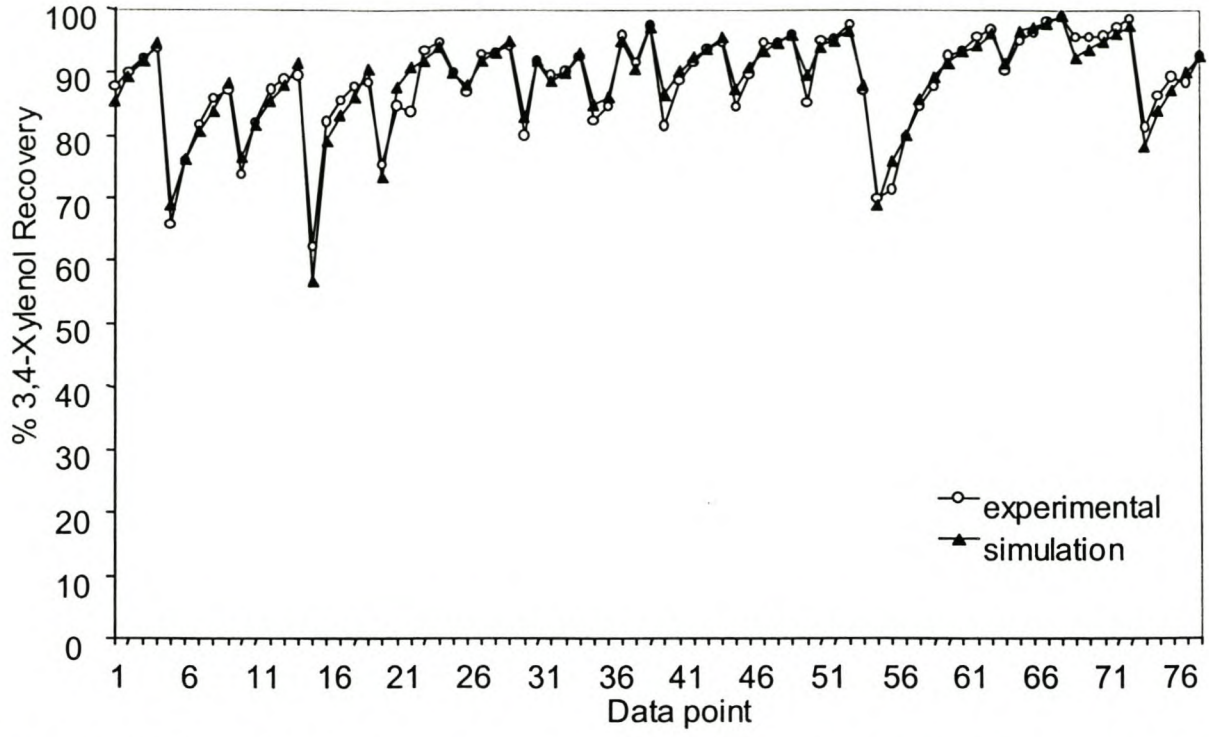


Figure 6.6-20. Comparison of experimental and simulated mass percentage recoveries of 3,4-xylenol in the solvent phase.

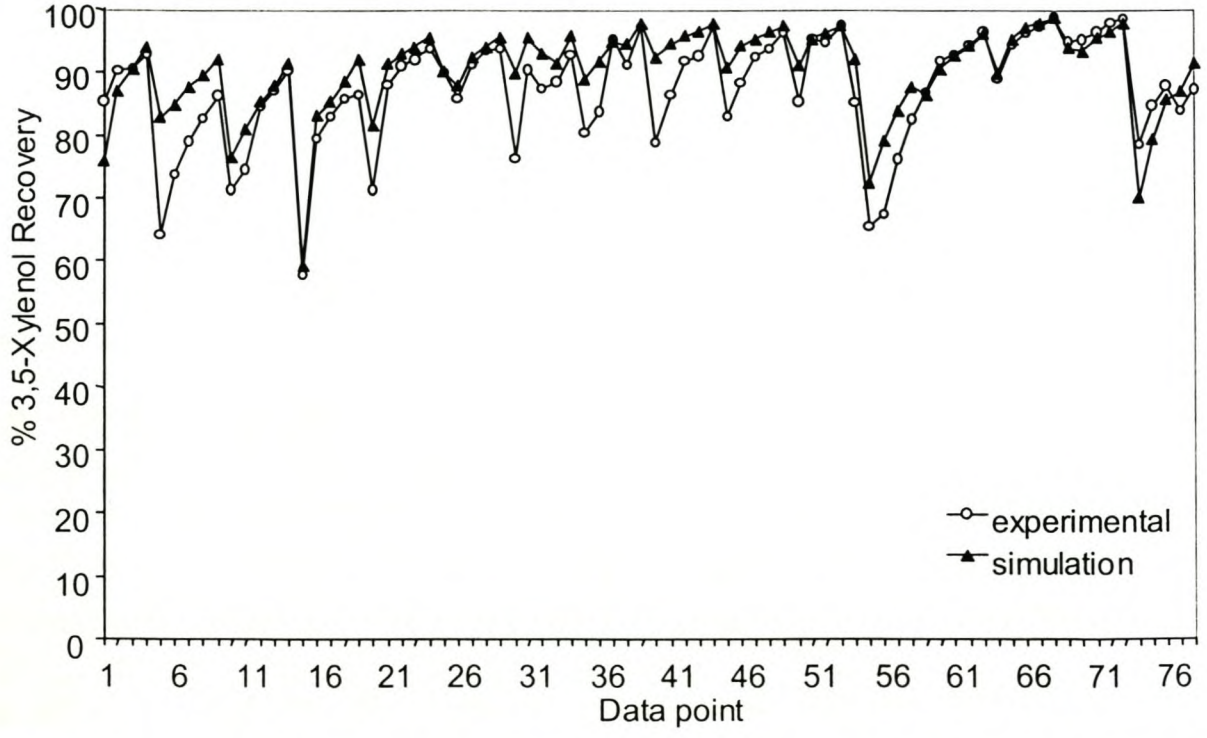


Figure 6.6-21. Comparison of experimental and simulated mass percentage recoveries of 3,5-xylenol in the solvent phase.

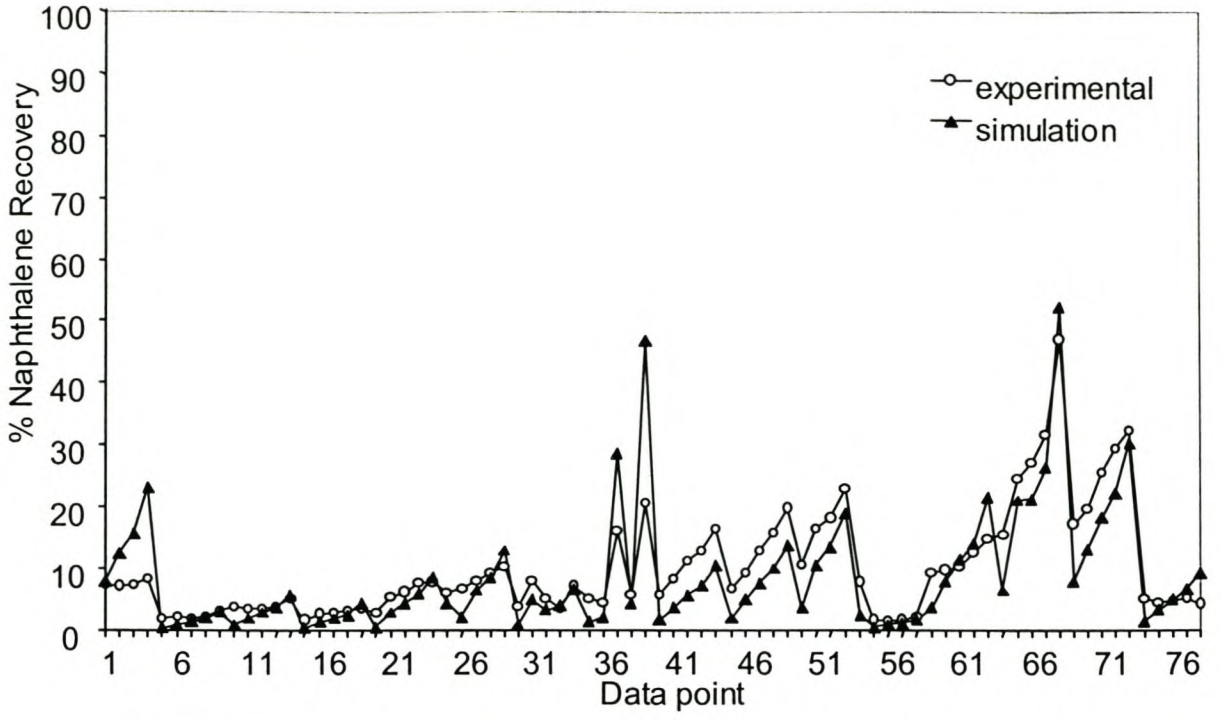


Figure 6.6-22. Comparison of experimental and simulated mass percentage recoveries of naphthalene in the solvent phase.

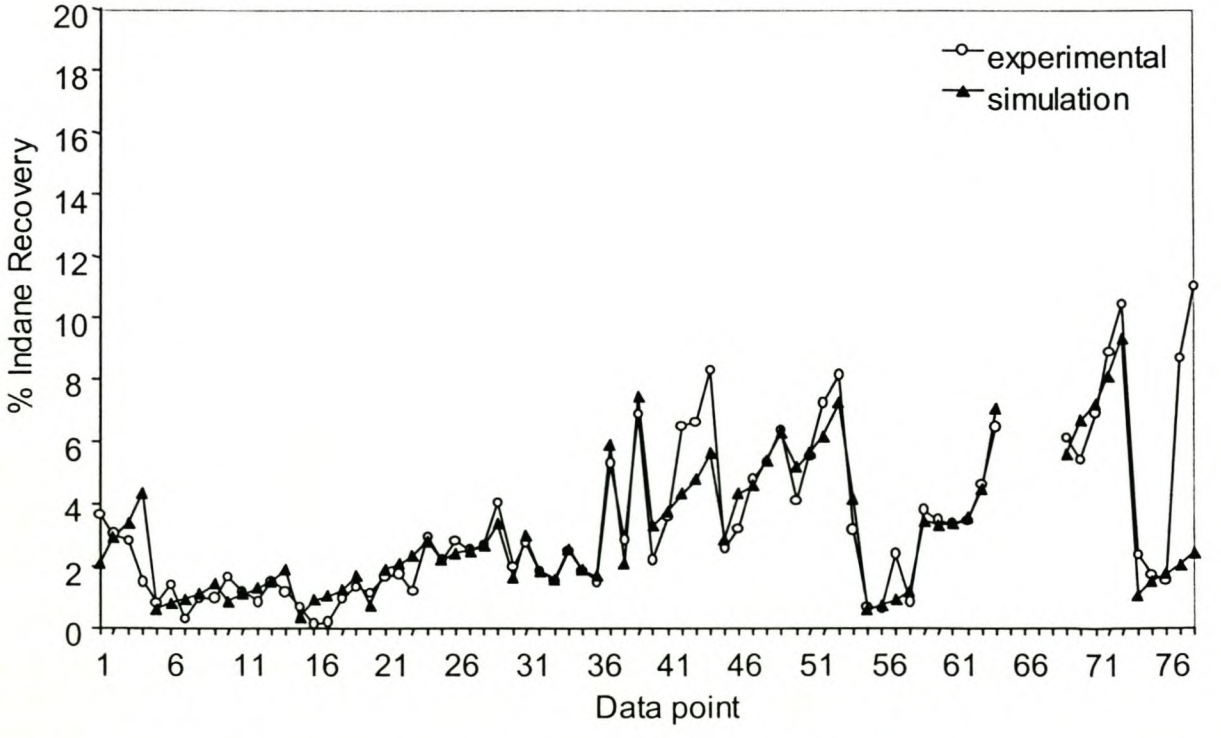


Figure 6.6-23. Comparison of experimental and simulated mass percentage recoveries of indane in the solvent phase.

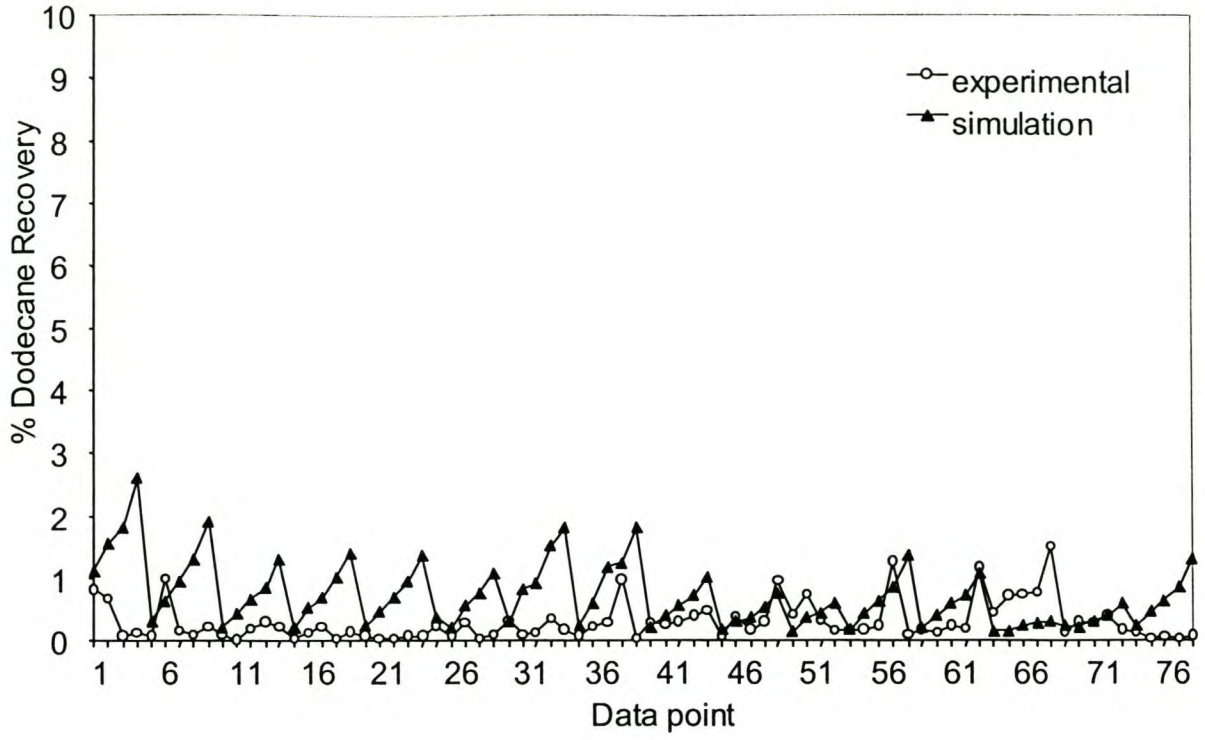


Figure 6.6-24. Comparison of experimental and simulated mass percentage recoveries of dodecane in the solvent phase.

Table 6-16. Absolute differences in experimental and simulated percentage recoveries of components in xylenol system.

Components	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]
Hexane	0.7	0.1	3.4
Water	0.1	0.0	0.5
Indane	0.7	0.0	8.6
Dodecane	0.5	0.0	2.5
Naphthalene	3.7	0.1	26.3
2,4-Xylenol	2.7	0.0	19.5
3,5-Xylenol	4.8	0.1	28.8
3,4-Xylenol	1.8	0.0	8.9
Triethylene Glycol	1.2	0.0	7.8

It can be seen from Figures 6.6-19 and 6.6-20 that the correlation achieved between the simulated and experimental 2,4- and 3,4-xylenol recoveries is excellent. Figures 6.6-21 to 6.6-23 show that the while the correlation between the values of the simulated and

experimental recoveries of 3,5-xylenol, indane and naphthalene is not as good, it is still satisfactory for most data points. Furthermore, the correlation in experimental and simulated trends exhibited is very good. As was the case with undecane in the m-cresol system, the predicted dodecane recovery shown in Figure 6.6-24 does not appear to correspond well with the experimental recoveries. As with undecane, this can be attributed to the extremely low solubility of dodecane in the solvent phase and, consequently, the very low recoveries thereof. It can be seen Table 6-18, that the maximum difference between experimental and predicted dodecane recoveries is only 2.5 percentage points.

It can further be seen from Table 6-18, as well as from Figures 6.6-19 to 6.6-24, that large discrepancies in the predicted and experimental component recoveries occur for all the feed components at certain data points. In the case of naphthalene and indane, the large discrepancies are found at data points corresponding to batch extractions carried out at hexane to feed ratios smaller than 1.5. The points for which the predicted and experimental recoveries of the xylenol isomers differ by more than five percentage points without exception correspond to data points obtained at solvent to feed ratios of 0.5.

In comparing the absolute differences between experimental and predicted component recoveries listed in Table 6-16 for the xylenol system and those listed for the other modelled systems in Tables 6-4, 6-7, 6-10 and 6-13, it is clear that the recoveries of the components in the xylenol system are predicted less accurately than those in the phenol, cresol, m,-p-cresol and cresol-aniline systems.

This can be attributed to the fact that the number of LLE data points available for regression relative to the number of unknown binary parameters to be determined is significantly lower for the xylenol system than for the other systems. The 66 unknown parameters in the m-cresol and xylenol systems were obtained through regression of 102 and 79 LLE data points respectively, while 89 LLE data points were available for the determination of the 56 unknown parameters in the phenol system. It can therefore be expected that the accuracy of the models based on the binary parameters determined for the phenol and m-cresol systems should be higher than that of the model based on the xylenol binary parameters.

Despite the fact that the results predicted for the xylenol system are not as accurate as those predicted for the phenol and m-cresol systems, it can be seen from Table 6-16 that, on average, they are still satisfactory. Also, as can be seen from Figures 6.6-19 to 6.6-23, the predicted trends in general correspond very well to the corresponding experimental trends.

6.6.4 TEG monomethylether system

It has been shown that the proposed NRTL parameters determined for a particular multicomponent system can successfully be used as a basis for an extended system. I.e. components can be added to the system and the model will be applicable. Another means of testing the validity of the model is to replace one component with another in a multicomponent system. Triethylene glycol was therefore replaced with triethylene glycol monomethylether (TEG monomethylether) in the phenol system. The resulting seven component system is that of hexane + water + mesitylene + 5-et-2-me-pyridine + aniline + benzonitrile + phenol + TEG monomethylether. Of the 56 parameters required to model this system, 42 were determined from the regression of the original phenol system. A series of 27 batch extractions was executed to generate LLE data for the determination of the remaining 14 binary parameters. These unknown parameters are those applicable to the component pairs containing TEG monomethylether.

The optimum parameters obtained through regression for the TEG monomethylether system are listed in Table 6-17. The weights of the component error terms in the goal function of the regression algorithm were specified as follows: hexane, 0.05; water, 0.05; mesitylene, 0.05; 5-et-2-me-pyridine, 1.0; aniline,;1.0, benzonitrile, 1.0; phenol, 1.0 and TEG monomethylether, 0.005.

Table 6-17. Optimum NRTL binary parameters for the system Hexane(1) + Water(2) + Mesitylene(3) + 5-Et-2-me-pyridine(4) + Aniline(5) + Benzonitrile(6) + Phenol(7) + TEG monomethylether(8). $\alpha_{ij} = \alpha_{ji} = 0.2$.

i	j	b_{ij}	b_{ji}	i	j	b_{ij}	b_{ji}
1	2	1883.5 *	3579.9 *	3	5	-139.9 *	6691.5 *
1	3	-1500.6 *	6366.4 *	3	6	1758.8 *	2330.3 *
1	4	2012.6 *	5960 *	3	7	-261.3 *	6656.4 *
1	5	481.5 *	503.2 *	3	8	569.0	-1575.8
1	6	2233.4 *	-131.2 *	4	5	-955.2 *	1674.8 *
1	7	1019.9 *	84.91 *	4	6	2469.8 *	2340 *
1	8	1302.5	285.8	4	7	1510.5 *	1105.1 *
2	3	351.0 *	750.5 *	4	8	979.0	1297.1
2	4	2996.2 *	5230.9 *	5	6	1044 *	-129.9 *
2	5	950.4 *	62.63 *	5	7	1630 *	-709 *
2	6	2602.8 *	6205.8 *	5	8	4774.5	-881.7
2	7	1403.2 *	-211.3 *	6	7	1057.7 *	996.5 *
2	8	1420.9	-428.9	6	8	5544.3	1087.1
3	4	1445.5 *	-199.3 *	7	8	7397.9	-821.8

*Fixed parameters determined by regression of the phenol system

Table 6-18 lists the absolute differences between the experimentally determined molar fractions of the components in both liquid phases and those predicted by means of simulations using the parameters listed in Table 6-17.

Table 6-18. Average, minimum and maximum absolute differences, δ_{Ave}, δ_{Min}, and δ_{Max} between experimental and simulated molar percentage concnentrations of components in the extract and hexane phases for the triethylene glycol monomethylether system.

	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]
Hexane	0.65	0.01	3.27	0.19	0.01	0.56
Water	0.44	0.04	1.40	0.02	0.00	0.07
Mesitylene	0.03	0.00	0.36	0.05	0.00	0.34
5-Et-2-me-pyridine	0.04	0.00	0.22	0.04	0.01	0.09
Aniline	0.03	0.00	0.16	0.01	0.00	0.06
Benzonitrile	0.03	0.00	0.11	0.03	0.00	0.17
Phenol	0.35	0.01	1.10	0.08	0.01	0.38
TEG monomethylether	0.33	0.00	2.00	0.07	0.00	0.40

It can be concluded from Table 6-18 that the proposed model accurately predicts the concentrations of the components in both the solvent and hexane phase. The correlation between simulated and predicted component recoveries is illustrated in Figures 6.6-25 to 6.6-29.

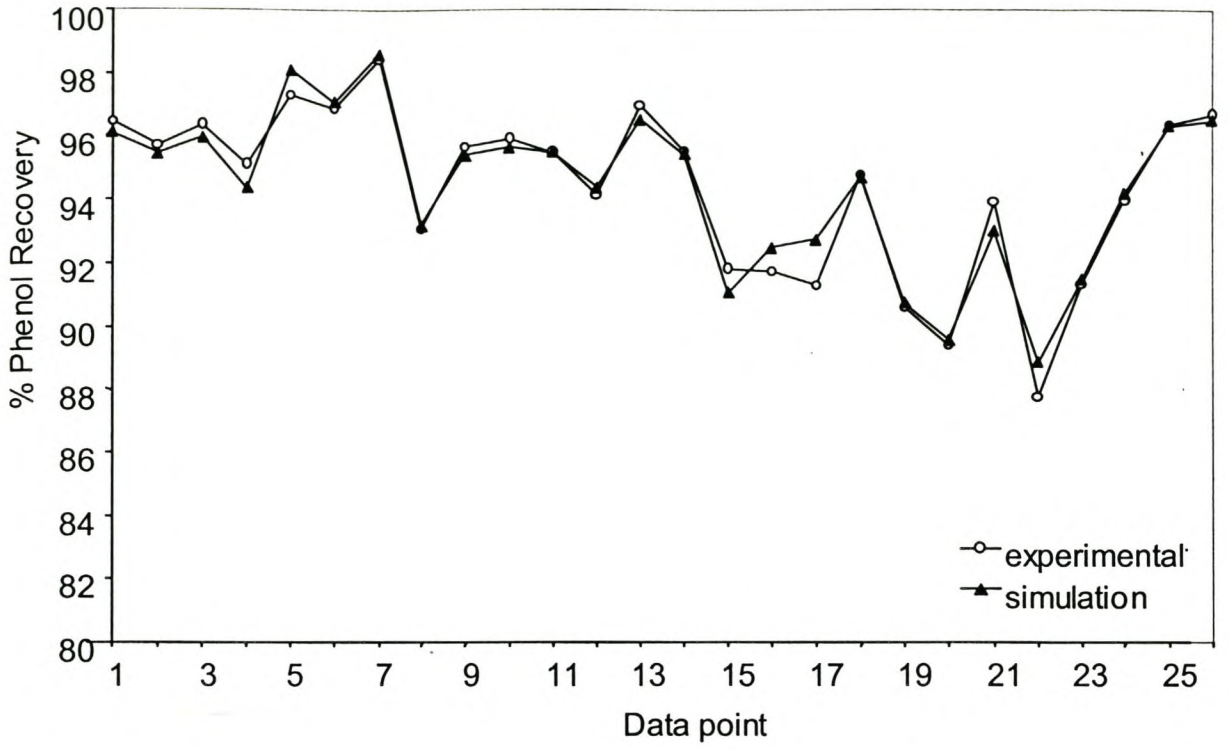


Figure 6.6-25. Comparison of experimental and simulated mass percentage recoveries of phenol in the solvent phase.

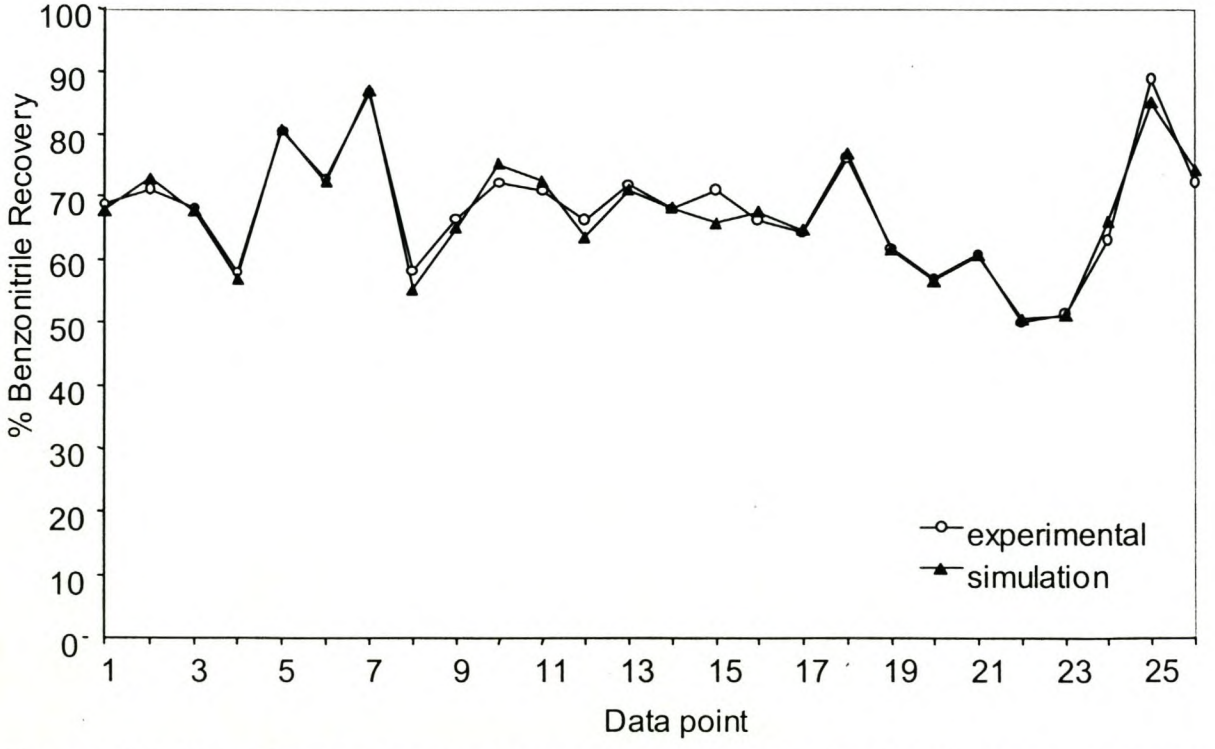


Figure 6.6-26. Comparison of experimental and simulated mass percentage recoveries of benzonitrile in the solvent phase.

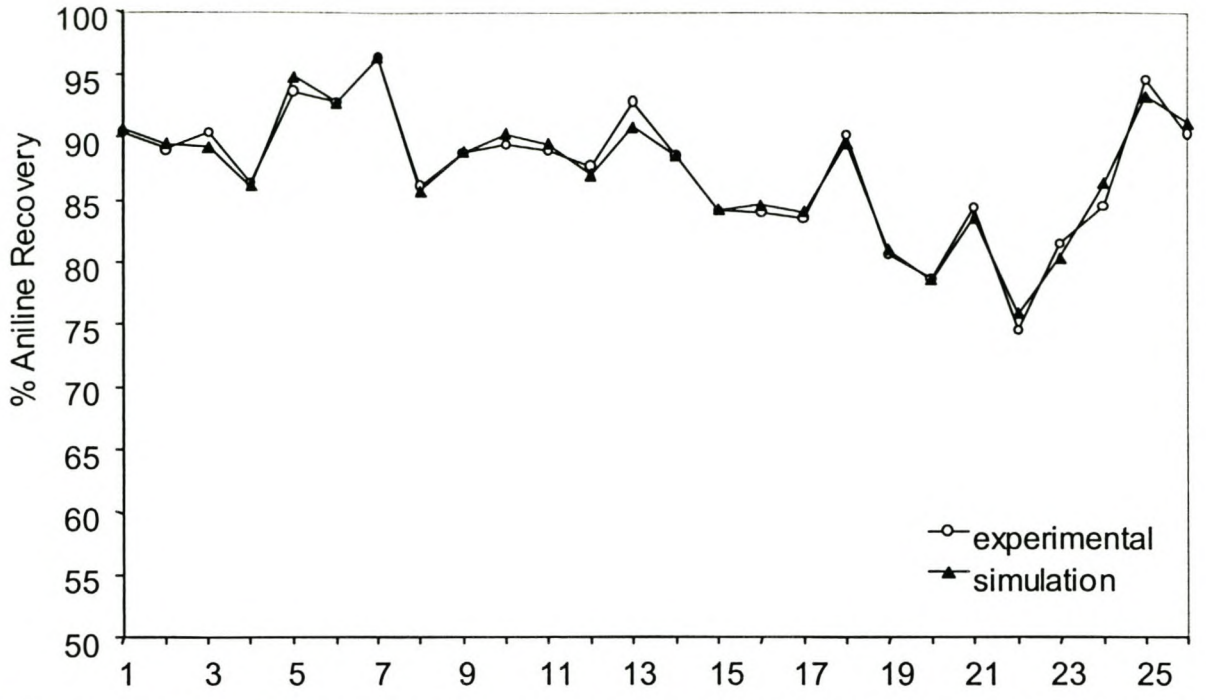


Figure 6.6-27. Comparison of experimental and simulated mass percentage recoveries of aniline in the solvent phase.

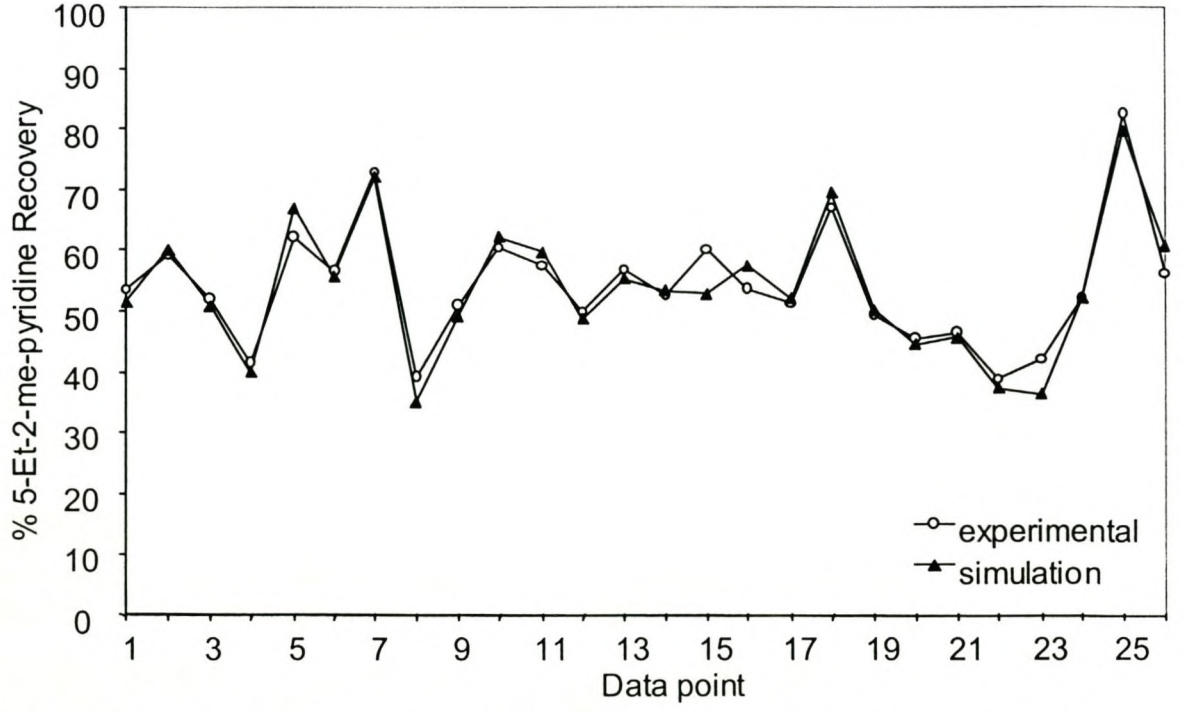


Figure 6.6-28. Comparison of experimental and simulated mass percentage recoveries of 5-et-2-me-pyridine in the solvent phase.

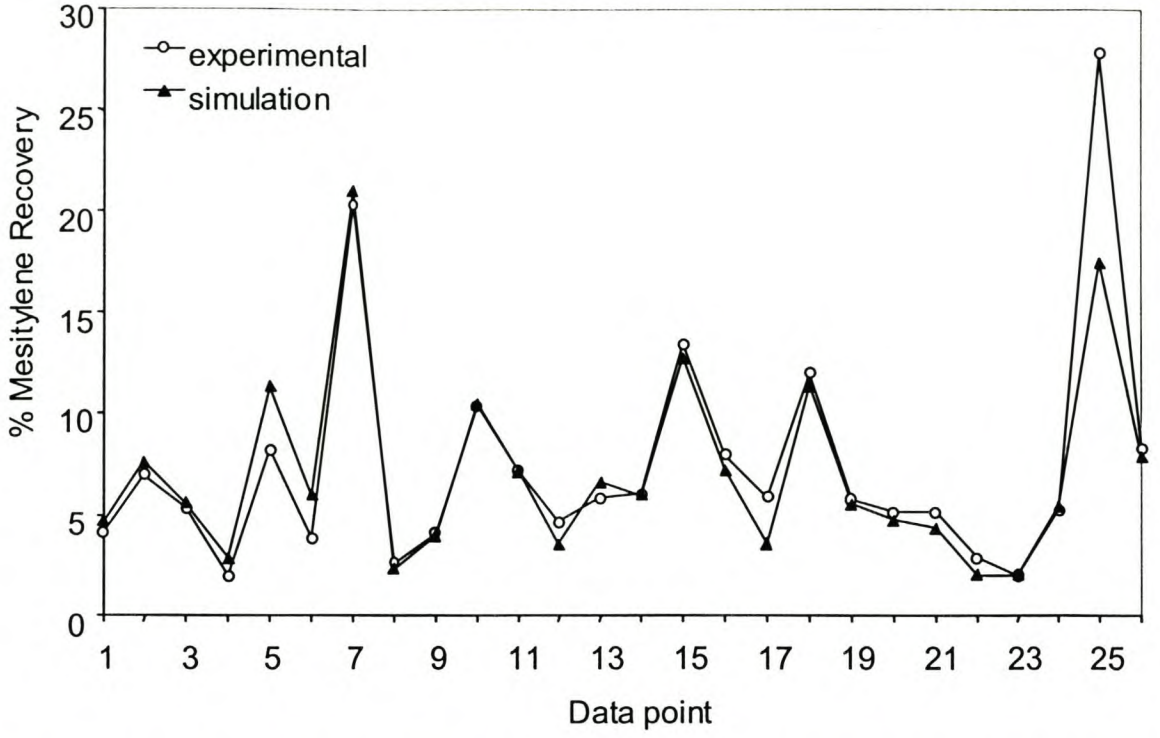


Figure 6.6-29. Comparison of experimental and simulated mass percentage recoveries of Mesitylene in the solvent phase.

Figures 6.6-25 to 6.6-29 show that not only the component recoveries, but also the trends exhibited by these recoveries are predicted very well by the proposed model. This is confirmed by the absolute differences between the experimental and simulated recoveries listed in Table 6-19.

Table 6-19. Average, minimum and maximum absolute differences, δ_{Ave}, δ_{Min}, and δ_{Max} between between experimental and simulated percentage recoveries of components in the TEG monomethylether system.

Component	δ_{Ave} [%]	δ_{Min} [%]	δ_{Max}[%]
Hexane	0.7	0.0	4.4
Water	0.04	0.0	0.2
Mesitylene	1.1	0.0	10.3
5-Et-2-me-pyridine	1.2	0.1	7.3
Aniline	0.7	0.0	2.1
Benzonitrile	1.4	0.2	5.4
Phenol	0.4	0.0	1.4
Triethylene Glycol	0.2	0.0	1.0

A comparison of Table 6-19 and Table 6-4 shows that the accuracy of the results predicted for the TEG monomethylether system compares very favourably to those predicted for the original phenol system.

It can therefore be concluded that the proposed model is valid, physically meaningful and can be used as a basis for the modelling of systems other than those for which it was determined. The NRTL model predicts the composition of the solvent and hexane phases, the component recoveries and trends exhibited in the data accurately for all the systems investigated. It can therefore be used with confidence as a basis for simulations for the optimisation of the proposed separation process.

CHAPTER 7. PILOT PLANT TESTS

7.1 Introduction

In liquid-liquid extraction systems, although solvent screening and preliminary evaluation is typically by means of batch extractions, single stage processes are seldom implemented on industrial scale, even for trivial separations.

Therefore, after verifying with batch extractions that a particular solvent system is effective for a given separation problem, the next step in the development thereof is the evaluation and optimisation of the proposed system on pilot plant scale in a multistage process.

On batch extraction scale, the combined solvent system of triethylene glycol, water and hexane has proven to be very effective for the separation of phenolic compounds from neutral oils and nitrogen bases. A countercurrent extraction column was therefore built in order to test the solvent system in a multistage process. Initial investigation of the process was done using a synthetic feed stream. The optimum solvent ratios and operating conditions determined with the synthetic feed stream were then applied to a typical industrial feed stream.

7.2 Multistage Countercurrent Extraction Column

7.2.1 Selection of Type of Extraction Column

The emphasis of the pilot plant tests is on the evaluation and optimisation of the proposed liquid-liquid extraction process. The first step in implementing this process is the selection of an appropriate extractor.

It has been ascertained that the separation of phenolic compounds from neutral oils and nitrogen bases is not a simple separation. Columns with low stage efficiency such as sieve-plate columns, packed columns and pulsed columns can therefore not be considered for this application.

Columns with rotating internals are typically used where a high degree of separation is required, as is the case in the process under investigation. While stage efficiency in an agitated column is not nearly that of a mixer-settler, a relatively large number of separation stages can be realised within a small overall height. The loading limit is generally lower than in pulsed columns, but this should not be a problem using the proposed solvent system as the density difference between hexane and triethylene glycol is significant. The proposed liquid-liquid system also exhibits no tendency towards emulsification.

A mixer-settler arrangement would also be appropriate for the application under investigation. However, mixer-settler arrangements entail disadvantages such as large holdup, high costs, large floor space and the need for interstage pumping. Consequently, a column extractor was selected for the pilot plant tests.

The agitated column chosen for the pilot plant tests is an adaptation of the Kühni column, which was discussed in Chapter 2. As is the case in the Kühni column, the mixing element in the pilot plant extraction columnis a double-entry radial-flow shrouded turbine impeller. Perforated stator plates separate the mixing stages. However, whereas the Kühni column has only one perforated stator plate between successive mixing stages, the adapted column has two. This is shown in Figure 7.2-1.

By using double stator plates, a settling zone is created. Knitted wire mesh is installed between the stator plates to induce coalescence and settling of the dispersed phase liquid droplets. To further promote settling efficiency, each pair of stator plates is aligned in such a way that the holes of one plate are staggered in relation to those of the next plate. The droplets of the heavy dispersed phase can therefore not follow a straight-line path through the pair of stator plates, but have to change direction after passing through one stator plate in order to pass through the next stator plate (see Figure 7.2-1). The flow path of the droplet through the settling zone and, consequently, the retention time of the droplet in the settling zone is longer.

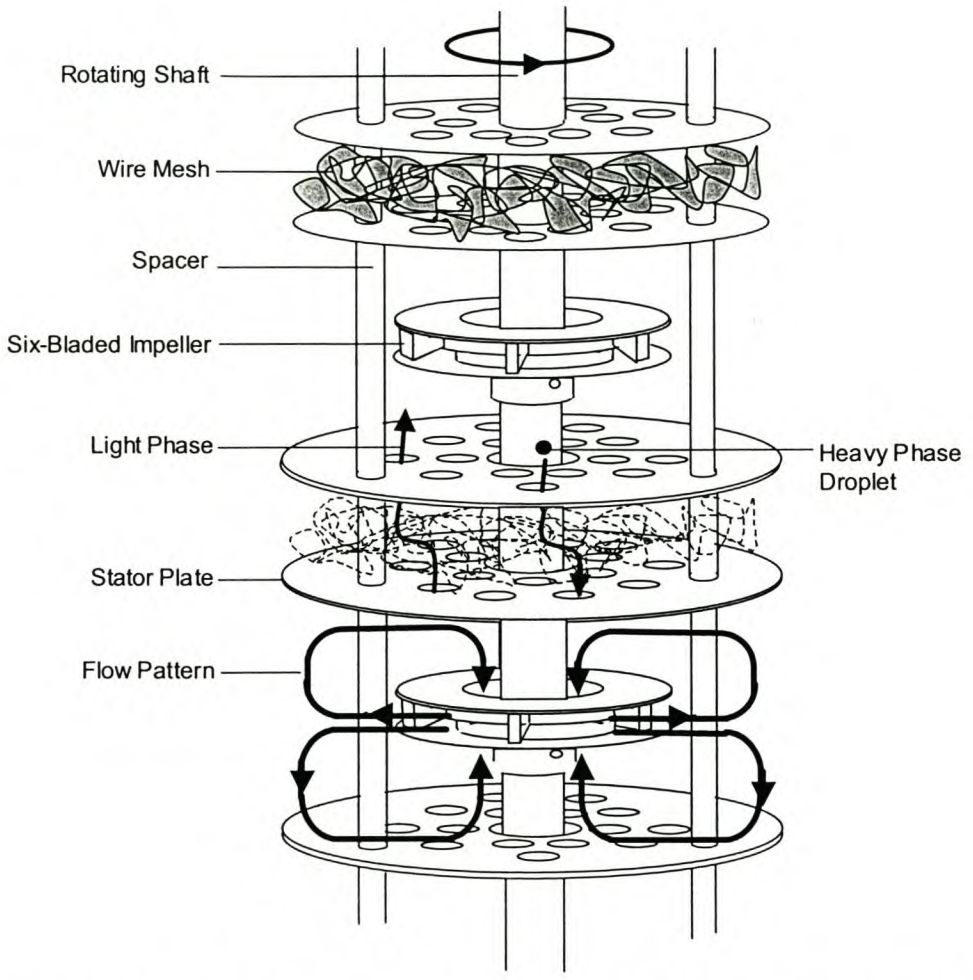


Figure 7.2-1. Detail of internal construction and flow patterns in the modified Kühni column.

7.2.2 Detailed Description of the Extraction Column

The extraction column used for the pilot plant tests was a glass column with an inner diameter of 75 mm and an overall height of 2.4 m. It consisted of six segments. The top five were 450 mm in length and the bottom segment 150 mm in length. 28 mixing stages were distributed between the top five segments. The heights of the mixing stages were between 52 and 57 mm. The height of the settling zones between the mixing stages was 17 mm. A diagram of the distribution of the mixing stages and settling zones is shown in Appendix E1. Mixing was by means of shrouded six-bladed turbine impellers 40 mm in diameter and 10 mm high. A detailed diagram of an impeller is shown in Appendix E2.

The impellers were mounted on a central shaft, which was rotated with a standard drill head. The rotational speed of the shaft could be varied by adjustment of the pulley ratio inside the drill head. The bearings anchoring the central shaft were mounted on plates

that positioned between successive column segments. These bearing plates had a free cross-sectional area of 45%. A detailed diagram of a bearing plate is shown in Appendix E3.

The equilibrium stage efficiency and throughput of a Kühni-type extraction column depend on the free cross-sectional area of the stator plates. An increase in the free cross-sectional area results in an increase in throughput of the column, but also in a decrease in equilibrium stage efficiency.

The relationship between stage efficiency and cross-sectional area of a standard Kühni column is illustrated in Figure 7.2-2.

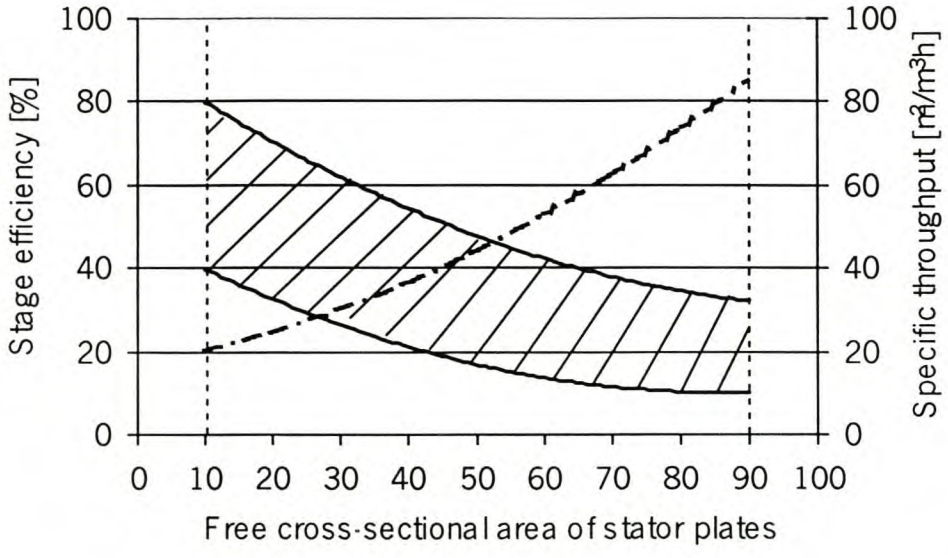


Figure 7.2-2. Influence of free cross-sectional area of stator plates on stage efficiency and specific throughput of a standard Kühni column [16].

The free cross-sectional area of the stator plates for the pilot plant extraction column was 36% of the column cross sectional area, which, according to Figure 7.2-2, corresponds to an equilibrium stage efficiency in the range of 25% to 55% and a specific throughput of approximately 33 m^3/m^2h. A standard Kühni column with an inner diameter of 75 mm and a stator plate free cross-sectional area of 36%, should therefore be capable of handling a total throughput of up to 145 litres per hour. Due to the extra stator plate between the mixing stages, the throughput of the modified column should be lower, and the equilibrium stage efficiency higher than that of a standard Kühni column. A detailed diagram of a stator plate is given in Appendix E4.

The pilot plant extraction column was configured for countercurrent extraction with the light phase as the continuous phase and the heavy phase as the dispersed phase. The light phase entered the column immediately below the stator plate bounding the lowest

mixing stage in the column. The heavy phase entered at the top of the column in the unmixed zone above the top mixing stage. The feed stream could enter the column at the top with the solvent stream or at four additional points distributed evenly among the four top column segments. The unmixed zone at the top of the column was approximately 77 mm in height and was packed with wire mesh in order to prevent entrainment of the heavy phase droplets entering the column. The light phase exited the column approximately 150 mm above the entrance point of the heavy phase. The exit point of the light phase and entrance point of the heavy phase were situated on opposite sides of the column.

The exit point of the heavy phase was at the bottom of the column. The stator plate bounding the lowest mixing stage was positioned approximately 70 mm from the bottom of the second lowest column segment. The lowest column segment was unmixed. I.e. a settling zone of approximately 220 mm was created at the bottom of the column. The interface between the heavy and light phases was maintained in this settling zone. The level of the interface, which should ideally be as high as possible in the settling zone in order to allow complete phase disengagement and the attainment of equilibrium between the two phases, was controlled by manipulation of a control valve on the exit line of the heavy phase.

The performance of the described extraction column depends on parameters such as the optimum impeller rotation speed, position of the feed entry point and solvent ratios. These parameters were optimised by means of simulations and pilot plant tests based on a synthetic feed stream.

7.3 Synthetic Feed Stream

The synthetic feed stream used for pilot plant tests consisted of aniline, o-tolunitrile , m-cresol and p-cresol.

In the batch extraction tests it was found that aromatic amines and nitriles are the most difficult types of components to separate from phenolic compounds. Aniline and o-tolunitrile were therefore included in the synthetic pilot plant feed in order to represent the aromatic amines and nitriles respectively.

m-Cresol was selected to represent the phenolic compounds. It was chosen in preference to phenol for two reasons. Firstly, the recovery of m-cresol is more sensitive to changes in the various solvent ratios than is the recovery of phenol. The optimum solvent ratios with regard to phenolic recovery can therefore be more clearly determined with m-cresol than with phenol. Secondly, m-cresol is a liquid at ambient temperature, whereas phenol is a solid. The handling of m-cresol is therefore much easier than that

of phenol. A mixture of the m- and p-cresol isomers was used instead of pure m-cresol since the isomer mixture was both significantly less expensive as well as more readily available than the pure isomers.

The composition of the synthetic feed stream was varied over the range of pilot plant tests. The concentrations of aniline and o-tolunitrile, while orders of magnitude higher than would be the case in industrial feed streams, were very low in comparison to the cresol isomers for all the pilot plant tests.

7.4 Process Description

A brief description of the proposed separation process including solvent recovery is required in order to provide the context for the pilot plant tests. A more detailed description of the process can be found in Section 8.2.

The schematic flow diagram for the proposed process is shown in Figure 7.4-1.

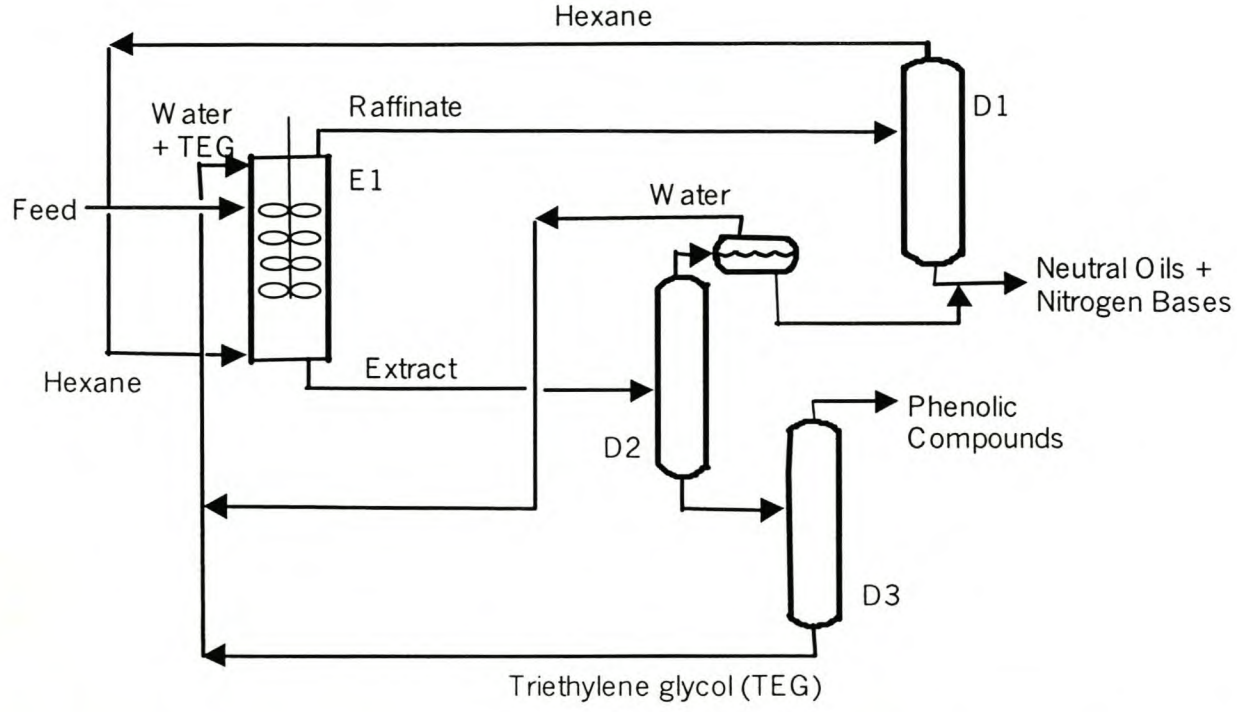


Figure 7.4-1. Schematic flow diagram for proposed separation process including solvent recovery. E1: Multistage extraction column; D1: Hexane recovery dolumn; D2: Water recovery column; D3 Solvent recovery colunm (patented by Nieuwoudt and Venter[93], priority date 9 October 1997).

The feed stream to the extraction column, E1, consists of a mixture of phenolic compounds, neutral oils and nitrogen bases. The solvent stream, consisting of triethylene glycol and water, enters the extraction column at the top along with the feed stream, while the countersolvent stream, consisting of hexane, enters the extraction column at the bottom. The hexane phase is the light continuous phase and moves upwards through the column while solvent phase is the heavy dispersed phase and moves downwards. The components of the feed stream are distributed between the two phases by means of countercurrent extraction. The resulting raffinate and extract phases exit the top and bottom of the column respectively.

Having exited the extraction column, the countersolvent phase, consisting of hexane, the neutral oils, nitrogen bases and traces of the phenolic compounds, water and triethylene glycol is fed to the hexane recovery column, D1. In this column, the hexane (bp. 68°C) and any water present (bp. 100°C) are removed as the overhead product stream and recycled to the extraction column. The considerably higher-boiling neutral oils, nitrogen bases, phenolic compounds and triethylene glycol in the raffinate (boiling points in excess of 160°C) are removed as the bottoms product.

The solvent phase leaving the extraction column consists of triethylene glycol, water, the bulk of the phenolic compounds in the original feed mixture and traces of neutral oils, nitrogen bases and hexane. It is fed to the water recovery column, D2, where the water and any residual hexane is removed as the overhead product under vacuum. A portion of the nitrogen bases, neutral oils and, to a lesser extent, phenolic compounds are removed as azeotropes with the water. The distillate of the water recovery column therefore contains both water-soluble and water-insoluble organic compounds. The aqueous and organic layers of the distillate may either be separated and the aqueous phase recycled to the extraction column, or the distillate may be washed with a bleed stream from the distillate stream from the hexane recovery column. This stage of the process is discussed in more detail in Section 8.2.

The phenolic compounds, triethylene glycol and any neutral oils and nitrogen bases still present in the extract phase are recovered as the bottoms product of the water recovery column and fed to the solvent recovery column, D3. The phenolic compounds, along with any residual neutral oils and nitrogen bases, are removed as distillate. This distillate stream is the final phenolic product stream. The triethylene glycol is recovered as the bottoms product and is added to the overhead stream from the water recovery column and recycled to the extraction column.

7.5 Pilot Plant Setup and Operation

In the pilot plant tests, the multistage countercurrent extraction column, E1, and hexane recovery column, D1, were operated continuously. A schematic diagram of the pilot plant setup for the continuous liquid-liquid extraction and hexane recovery process is shown in Figure 7.5-1.

Triethylene glycol, water and the feed components were mixed in the ratio required to obtain the desired solvent to feed and water to solvent ratios for a proposed test. The resulting homogenous mixture was thoroughly mixed. It was then pumped to the top of the extraction column using a positive displacement pump. The hexane was pumped with a positive displacement pump to the bottom of the extraction column. The hexane to feed ratio required for a proposed test was obtained by adjusting the frequency and stroke-length of the solvent and feed pump as well as the stroke-length of the hexane feed pump.

The volumetric flowrate of the combined solvent and feed stream was measured at the applicable pump stroke-length and frequency for each test. The volumetric flow rate of the hexane stream was measured using a calibrated rotameter.

Both the combined solvent and feed stream and hexane stream were heated by means of cartridge heaters prior to entering the extraction column. The duty of the cartridge heaters, and consequently the temperature of the streams entering the extraction column, could be varied by varying the current flowing through the heaters. The temperatures of the process streams entering the extraction column were measured with an accuracy of within $\pm 1.0°C$ with standard type K thermocouples. The temperature of the liquid inside the extraction column was similarly measured at the midpoint of the column. The thermocouples were tested for accuracy in the temperature range 0 to 100°C prior to installation.

The raffinate stream exiting the top of the extraction column flowed directly to the hexane recovery column. The flow rate of the raffinate stream could not be measured accurately as the hexane recovery column operated at a marginally lower pressure than did the extraction column. Therefore, despite the fact that the sampling valve was inserted below the level of line connecting the two columns, a portion of the raffinate stream was siphoned directly to the hexane column and did not flow under gravity through the valve.

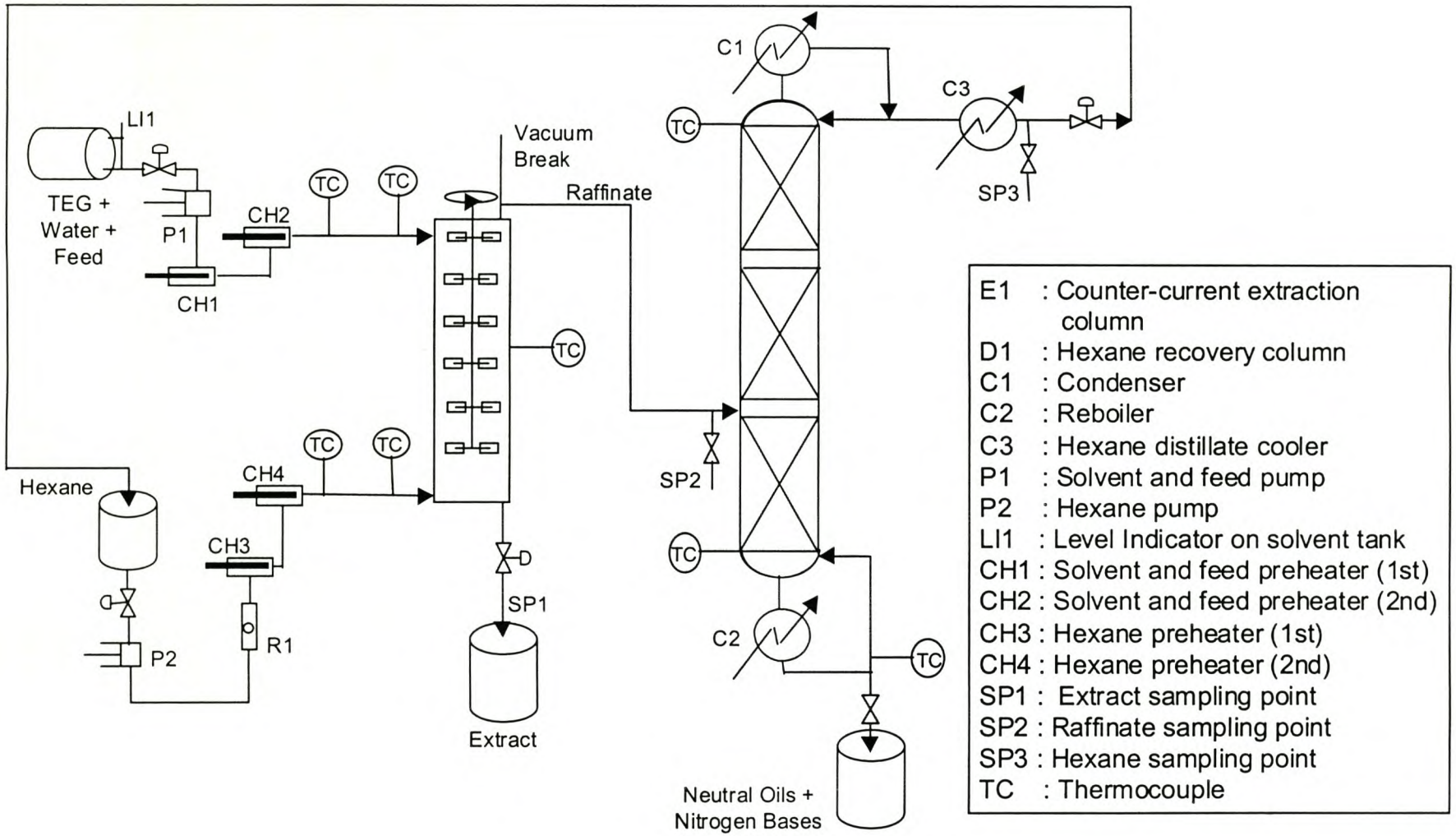


Figure 7.5-1. Process flow diagram of experimental setup for pilot plant tests using the synthetic feed stream

The hexane was recovered as distillate from the raffinate phase in a standard 200 mm glass distillation column packed with three 824 mm sections of Sulzer 350Y packing. The feed point to the column was above the first section of packing. The condenser was water-cooled. The temperature of the distillate was maintained at 68.5°C ± 1.5°C at atmospheric pressure.

After exiting the condenser, the recovered hexane was cooled further in a water-cooled heat exchanger before returning to the covered hexane feed tank.

The extract phase exited the extraction column at the bottom and was collected in a glass container for further processing. The flowrate of the extract stream was regulated with a control valve so as to maintain the required interface level at the bottom of the extraction column. Since the level of the interface fluctuated the volumetric flowrate of the extract phase also varied, which meant that the extract flowrate could not be accurately measured.

The extraction and hexane columns were operated continuously for a minimum of two hours in order to achieve steady-state conditions before samples of the combined solvent and feed, extract and raffinate streams were drawn. Both the extract and raffinate streams were sampled as they exited the extraction column. Large enough samples were taken to minimise the influence of small fluctuations in the process streams.

The pilot plant tests carried out with the synthetic feed stream did not include water recovery or solvent recovery steps. The water and solvent (TEG) were continuously fed with the synthetic feed mixture. Extract samples were taken to evaluate the water and solvent recovery steps on laboratory scale.

7.5.1 Analysis and Calculation

All the components in the extraction system, with the exception of water, were analysed by means of gas chromatography. The water concentrations of the combined feed and solvent stream, extract stream and raffinate stream were determined by means of Karl Fischer volumetric titrations. The analytical equipment and procedure used was identical to that discussed in Chapter 5 for the batch extractions carried out on the synthetic phenol, m-cresol and xylenol feed streams.

It was previously noted that the extract and raffinate flowrates could not be accurately measured. These flowrates were therefore calculated according to the water component balance and total mass balance over the extraction column.

I.e.

$$x_w^F F + x_w^H H = x_w^I E + x_w^{II} R \qquad (7.5\text{-}1)$$

and

$$F + H = E + R \qquad (7.5\text{-}2)$$

Where

x_w	:	analytically determined mass fraction of water
F	:	measured mass flowrate of combined solvent and feed stream
H	:	measured mass flowrate of hexane stream
E	:	mass flowrate of extract stream
R	:	mass flowrate of raffinate stream

Superscripts:

F	:	Feed stream
H	:	Hexane stream
I	:	Extract stream
II	:	Raffinate stream

The mass fraction of water in the hexane phase was zero for all the pilot plant tests and the mass fractions of water in the feed, extract and raffinate streams could be measured accurately as could the mass flowrates of the feed and hexane streams. The mass flowrates of the extract and raffinate streams could therefore be calculated.

7.5.2 Results of first pilot plant run

When evaluating the results obtained for the synthetic feed stream and optimising the performance of the extraction column, the difference in composition of the synthetic feed stream and an industrial feed stream must be borne in mind. So too must the subsequent solvent recovery unit operations.

The composition of the feed stream used in the pilot plant tests was varied. However, in all cases the cresol isomers accounted for approximately 90% of the feed stream, aniline approximately 10% and o-tolunitrile approximately 0.5 to 0.7%.

It is important to emphasise the fact that the percentage of aniline in the synthetic feed stream is orders of magnitude higher than that encountered in an industrial feed stream. It was noted in Section 3.5 that the combined percentage of the aromatic nitriles and amines in a typical industrial feed stream is less than 2%. The results obtained from

batch extractions performed on the phenol and m-cresol feed streams showed that the removal of aniline from the extract phase is considerably more difficult than the removal of the aromatic nitriles, pyridines, neutral oils or the higher substituted aromatic amines, such as o-toluidine. The residual concentration of aniline in the extract phase obtained for the synthetic feed stream will be considerably higher than will be the case for an industrial feed stream.

Another fact that must be taken into consideration is that residual aromatic nitriles and amines are typically removed from commercial phenolic product streams by means of steam stripping. It can therefore be expected that a significant portion of the aromatic amines and nitriles remaining in the extract phase will be removed as distillate in the water recovery column after extraction. The significance of this fact is twofold. Firstly, a higher water to solvent ratio than that which is optimal for the extraction process alone may be justified as the subsequent removal of this water will result in purification of the phenolic product. Also, the purity of the phenolic product with respect to nitrogen bases and aromatic nitriles in the extract phase exiting the extraction column need not fulfil the specifications for the final product purity, as the purity will improve during water recovery.

The first pilot plant test was carried out under the following conditions:

- Mass composition of feed: 53.3% m-cresol, 35.6% p-cresol,10.4% aniline and 0.7% o-tolunitrile
- Solvent to feed mass ratio: 2.6
- Hexane to feed mass ratio: 5.2
- Water to solvent mass ratio: 0.3
- Feed entry point at the top of the extraction column with the solvent mixture
- Combined solvent and feed stream temperature before entering column: 37.5°C
- Hexane temperature before entering column: 39.8°C
- Rotation speed of impellers: 260 rpm
- Total volumetric throughput of both liquid phases: 60 litres per hour

The results obtained were as follows:

- Percentage of feed aniline remaining in the extract phase: 79.7%
- Percentage of feed o-tolunitrile remaining in the extract phase: 10.9%
- Combined percentage recovery of m-cresol and p-cresol: 94.7%
- Percentage purity of extract on a triethylene glycol- and water-free basis: 90.9%

The resulting phenolic product purity is clearly not satisfactory. Also the recovery of aniline in the extract phase is extremely high. Even assuming that the optimum solvent

ratios are not employed, it is clear that the separation is not nearly what could be expected, given the high separation factors obtained for phenol with respect to aniline and especially m-cresol with respect to o-tolunitrile. This could be attributed to the fact that in the batch extractions the solvent and hexane phases reached equilibrium, while this is by no means guaranteed in the pilot column. The possibility exists that the process under investigation is mass transfer limited rather than equilibrium limited. I.e. a satisfactory separation could possibly be achieved if equilibrium was reached for each separation stage, but as mass transfer between the two phases is slow, this is not realised.

Therefore, before proceeding with further pilot plant tests, a series of batch extractions were performed in order to gain a clearer understanding of the hydrodynamic behaviour of the proposed solvent system.

7.5.3 Hydrodynamic tests.

The influences of parameters such as water to solvent ratio, temperature and shake-up time on the settling rate of the solvent and hexane phases were investigated. So too was the effect of settling time and temperature on the removal of aniline and o-tolunitrile from the solvent phase. Cyclohexane was also investigated as an alternative countersolvent to hexane.

The high surface tension of water inhibits coalescence. Consequently, the water content of the solvent phase is expected to have an influence on the settling rate of the dispersed solvent phase. A series of five batch extractions with water to solvent ratios of 0.0, 0.06, 0.3, 1.0 and 1.5 respectively were therefore carried out at ambient temperature (approximately 18°C). The solvent to feed ratio and hexane to feed ratio were constant at 3.0 and 5.0 for all five batch extractions. A homogenous feed mixture consisting of 48.5% m-cresol, 32.7% p-cresol, 13.5% aniline and 5.4% o-tolunitrile was used for the extractions as well as for all subsequent hydrodynamic tests.

The feed mixture, water, triethylene glycol and hexane were separately added to five separating funnels. The funnels were then simultaneously shaken for 1 minute before allowing the contents to settle. The rate at which the heavy solvent phase settled was observed. It was noted that the higher the water to solvent ratio of a system, the lower the rate of phase separation. This was especially noticeable for the systems with high water to solvent ratios of 1.0 and 1.5. The difference in settling rate between the batch extraction carried out with a water to solvent ratio of 0.06 and that of the batch extraction containing no water, was negligible.

It can therefore be concluded that for the proposed solvent system of triethylene glycol, water and hexane, the impact of the water to solvent ratio on efficiency of phase separation is negligible at very low water to solvent ratios and significant at water to solvent ratios higher than 0.3.

The effect of settling time on the separation achieved between the phenolic compounds and nitrogen bases was investigated next. Two batch extractions were carried out at a solvent to feed ratio of 3.0, hexane to feed ratio of 4.0 and water to solvent ratio of 0.0. The feed mixture was the same as was used in the previous set of batch extractions. The feed, triethylene glycol and hexane were shaken at ambient temperature for 1 minute. One separating funnel was allowed to stand for 24 hours in order to ensure that equilibrium was reached, while the other was drained after a settling time of two minutes. The resulting phases of both extractions were then analysed. The results are given in Table 7-1.

Table 7-1. Effect of settling time on percentage recovery of m-,p-cresol isomers and mass of aniline and o-tolunitrile remaining in the extract phase at 18°C.

	Mass percentage recovery of components[%]			Nitrogen base loading of hexane. [mg/g]	
Settling time	m-Cresol + p-Cresol	Aniline	o-Tolunitrile	Aniline	o-Tolunitrile
24 hours	96.3	92.1	66.7	2.0	4.1
2 minutes	97.2	94.2	72.6	1.3	3.8

It can be seen from Table 7-1 that a significant improvement in the removal of o-tolunitrile from the extract phase is obtained by allowing the system to attain equilibrium. The corresponding improvement in aniline removal, while significant with respect to the low overall removal of aniline, is very small with respect to the amount of aniline remaining in the extract phase.

The percentage of feed aniline remaining in the extract phase after a single extraction stage, which reached equilibrium, is 92.1%. The percentage of feed aniline remaining in the extract phase resulting from the multistage pilot plant extraction process is 79.7%. The solvent to feed ratio used in the pilot plant test is lower, and the water to solvent and hexane to feed ratios are higher than those applicable to the batch extraction. The percentage of feed aniline remaining in the extract phase should decrease both with a decrease in solvent to feed ratio and with an increase in the hexane to feed or water to solvent ratios. I.e. the solvent ratios used in the pilot plant column are more favourable for the removal of aniline from the solvent phase than are those used in the batch

extraction test. Despite these considerations, only 12.4% more aniline is removed in the multistage extraction than in the single stage extraction. It has been illustrated that allowing the extraction system to attain equilibrium does not significantly decrease the percentage of feed aniline remaining in the solvent phase. I.e. the poor removal of aniline in the pilot plant column cannot be attributed solely to the fact that the two liquid phases do not reach equilibrium at each separation stage. This is confirmed by the fact that the results obtained for o-tolunitrile do not reflect the same trends as do those obtained for aniline; the percentage of o-tolunitrile remaining in the extract phase is considerably lower at 10.9% after the multistage extraction process than it is at 66.7% after the single stage extraction process.

It can therefore be concluded that the very low removal of aniline from the extract phase is due to the interaction of aniline with the solvent and hexane phases, not the hydrodynamic conditions in the extraction column.

A possible reason for the limit to aniline removal by hexane is the fact that aniline is only sparingly soluble in hexane, especially at low temperatures. A series of solubility tests were carried out in order to investigate the effect of temperature on aniline solubility in hexane. It was found that at 18°C, 38°C and 55°C respectively, the capacity of hexane for aniline was 0.06, 0.13 and 0.18 grams of aniline per gram of hexane.

A further set of three batch extractions was therefore carried out at 40°C. The hexane to feed and solvent to feed ratios in these tests were 4.0 and 3.0 respectively. The water to solvent ratio was 0.0, 0.05 and 0.1 respectively. The purpose of these tests was twofold. Firstly, the effect of temperature on the removal of aniline could be investigated. Secondly, the effect of the water to solvent ratio on the settling rate could be determined at a higher temperature than ambient temperature. It was shown in Table 7-1 that the percentage of o-tolunitrile remaining in the extract phase is significantly lower at equilibrium conditions than at conditions where the solvent phase has not fully settled. An increase in the settling rate results in increase in the rate at which the system attains equilibrium. Therefore, after a certain settling time interval has elapsed, a system with a higher settling rate will be closer to attaining equilibrium than one with a lower settling rate. I.e. the percentage of o-tolunitrile remaining in the solvent phase after a certain settling time has elapsed will decrease as the settling rate is increased.

The hexane, triethylene glycol and water were added to the separating funnels and placed in a water bath at 40°C for half an hour. The feed mixture was placed in the water bath in a separate container. After the solvents in the separating funnels and the feed had reached a temperature of 40°C, the feed was added to the separating funnels, which were shaken for 30 seconds and allowed to settle for 2 minutes before being sampled. As was the case at ambient temperature, there was no discernible difference

in the settling rates of the systems with water to solvent ratios of 0.05 and 0.0. The settling rate of the system with a water to solvent ratio of 0.1 was however marginally lower.

The separation results of the batch tests with the water to solvent ratios of 0.0 and 0.1 are given in Table 7-2.

Table 7-2. Effect of water to solvent ratio on separation efficiency at a temperature of 40°C and settling time of two minutes.

	Mass percentage recovery of components[%]			Nitrogen base loading of hexane. [mg/g]	
Water to Solvent ratio	m-Cresol + p-Cresol	Aniline	o-Tolunitrile	Aniline	o-Tolunitrile
0.0	95.2	88.6	65.7	3.94	4.3
0.1	93.5	86.1	63.3	3.95	5.2

From Table 7-2 it can be concluded that, although the settling rate is lower for the batch extractions with a higher water to solvent ratio, the separation efficiency is nonetheless marginally higher. This can be attributed to the fact that the solubility of aniline and o-tolunitrile in the hexane phase relative to the solvent phase is increased by the increase in the water to solvent ratio. Thus, although the system containing more water is further from equilibrium than the system containing less water, the difference in the equilibrium conditions is large enough that the separation efficiency is higher.

It can also be seen from a comparison of Table 7-1 and Table 7-2 that, while the loading of hexane with aniline at 40°C is approximately double that at 18°C, the increase in the loading of hexane with o-tolunitrile is negligible. This is due to the fact that o-tolunitrile is already miscible with hexane at low temperature. I.e. an increase in temperature cannot lead to a significant increase in the solubility of o-tolunitrile in hexane.

In order to further investigate the effect of the capacity of the countersolvent on aniline removal, two batch extractions were performed under conditions approaching infinite dilution, using hexane and cyclohexane respectively as countersolvents. The feed mixture was the same as that used in the previous hydrodynamic tests. The solvent to feed ratio, countersolvent to feed ratio and water to solvent ratio were approximately 45, 55 and 0.1 respectively. The ratio of triethylene glycol to countersolvent was identical to that corresponding to a solvent system in which the solvent to feed ratio and hexane to feed ratio are 3.0 and 4.0 respectively. The components were added to the separating funnels, shaken for 1 minute and allowed to settle at 18°C for two hours. The resulting phases were analysed. As the masses of feed components used in these two batch extractions were extremely small, the experimental margin for error is greater than in a

typical batch extraction. An indication as to the effect of the countersolvent on the separation efficiency can however be obtained with reasonable certainty. The results are shown in Table 7-3.

Table 7-3. Effect of countersolvent on separation efficiency for conditions approximating infinite dilution at a temperature of 18°C.

	Mass percentage recovery of components[%]			Nitrogen base loading of countersolvent [mg/g]	
Countersolvent	m-Cresol + p-Cresol	Aniline	o-Tolunitrile	Aniline	o-Tolunitrile
Cyclohexane	89.8	91.9	54.7	1.8	4.9
Hexane	91.6	91.2	51.0	1.9	5.2

From Table 7-3 it can be seen that, despite the lower solubility of aniline in hexane, there is no noteworthy difference in the aniline recoveries achieved with hexane and cyclohexane. In fact, the separation efficiency achieved with hexane appears to be higher than that achieved with cyclohexane. A comparison of Table 7-4 and Table 7-3 indicates that an increase in the ratio of hexane to aniline by an order of magnitude does not result in a noticeable decrease in the percentage of aniline remaining in the hexane phase.

It can therefore be concluded that the capacity of the countersolvent for aniline is not the limiting factor in aniline removal. This is confirmed by the fact that, as was previously mentioned, the solubility of aniline in hexane at 38°C is 0.13 grams of aniline per gram of hexane. Despite this fact, it can be seen from Table 7-2 that, at 40°C, the solubility of aniline is only 4 mg / g in the hexane phase.

It can therefore be concluded that the affinity of anilne for the triethylene glycol in the solvent phase is too strong to permit the effective removal of aniline using countersolvents such as hexane and cyclohexane.

As cyclohexane yields results comparable to those obtained with hexane for systems that are allowed to reach equilibrium, the hydrodynamic behaviour of cyclohexane in comparison to that of hexane was investigated. It was reasoned that, should a system using cyclohexane as a countersolvent approach equilibrium conditions faster than one in which hexane is the countersolvent, the replacement of hexane with cyclohexane

would be justified as the stage efficiency of the extraction column with respect to the removal of o-tolunitrile from the extract phase would improve.

The settling rates of cyclohexane relative to those of hexane were therefore investigated. Four extractions were carried out at 18°C. In all four the solvent to feed ratio was 3.0 and countersolvent to feed ratio was 4.0. Two were carried out with cyclohexane at water to solvent ratios of 0.0 and 0.06 respectively, and two were carried out using hexane at corresponding water to solvent ratios. The separating funnels were simultaneously shaken for 1 minute and allowed to settle. It was observed that the liquid-liquid systems containing hexane settled faster at both water to solvent ratios. While the difference in the settling rate of the hexane extractions was scarcely discernible, the cyclohexane extraction with a water to solvent ratio of 0.1 settled noticeably slower than the one executed with a water to solvent raito of 0.0. It can therefore be concluded that the settling rates of solvent systems containing cyclohexane are more sensitive to the water content of the solvent than are those containing hexane.

The final parameter that was investigated was the effect of shake-up time on the settling efficiency of the proposed solvent system. This was done in order to gain an understanding of the effect of the rotation speed of the impellers in the extraction. Three batch extractions were carried out at 18°C at a solvent to feed, hexane to feed and water to solvent ratio of 3.0, 4.0 and 0.05 respectively. The length of time for which each separating funnel was shaken was 1, 5 and 15 minutes respectively. The shaking was executed in such a way that the shaking ended simultaneously. The contents of the separating funnels were allowed to settle for 1 minute before being drained. The resulting phases were analysed. The results obtained are listed in Table 7-5.

Table 7-5. Effect of shake-up time on separation efficiency at a temperature of 18°C and a settling time of 1 minute.

Time [min]		Mass percentage recovery of components[%]			Nitrogen base loading of countersolvent [mg/g]	
Shake-up	Settling	m-Cresol + p-Cresol	Aniline	o-Tolunitrile	Aniline	o-Tolunitrile
15	1	97.6	94.7	67.5	1.7	3.8
5	1	97.2	94.5	66.7	1.8	4.2
1	1	96.5	94.8	66.7	1.8	4.6

It was observed that, in all cases, the longer the separating funnel was shaken, the slower the rate of settling and disengagement of the liquid phases. As can be seen in Table 7-5 however, the effect of the varying settling rates on the separation efficiency is negligible, especially when compared to the corresponding effect of a small variation in

the water to solvent ratios. This conclusion was confirmed with a set of three batch extractions in which the water to solvent ratio was increased in successive tests from 0.05 to 0.1 to 0.3. The separating funnels were shaken for one minute and allowed to settle for one minute before being drained. The results obtained are given in Table 7-6.

Table 7-6. Effect of water to solvent ratio time on separation efficiency for a shaking and settling time of 1 minute.

W/S	Mass percentage recovery of components[%]			Nitrogen base loading of countersolvent [mg/g]	
	m-Cresol + p-Cresol	Aniline	o-Toluntirile	Aniline	o-Toluntirile
0.05	96.5	94.8	66.7	1.8	4.6
0.11	99.0	94.5	64.8	1.7	4.2
0.33	98.5	92.2	53.4	2.5	5.6

The results shown in Table 7-6 once again confirm that a higher water to solvent ratio than that which yields the optimum phenol-aniline and m-cresol-o-tolunitrile separation factors should be implemented to facilitate the removal of aniline and o-tolunitrile from the extract phase.

The following conclusions may be drawn from the hydrodynamic tests:

1. The rate of phase disengagement and rate of settling of the solvent phase decreases with an increase in the water to solvent ratio
2. The corresponding decrease in the recovery of both aniline and o-tolunitrile with an increase in the water to solvent ratio outweighs the negative effect of a decrease in the settling rates
3. The percentage of feed o-tolunitrile remaining in the extract phase can be significantly decreased if the solvent and hexane phases are allowed to reach equilibrium
4. The corresponding decrease in the aniline remaining in the extract phase is negligible
5. The capacity of hexane for aniline is not the limiting factor in the removal of aniline from the extract phase, rather the high affinity of aniline for triethylene glycol is
6. A marginally better separation of m- and p-cresol from aniline and o-tolunitrile as well as a higher recovery of the cresol isomers, may be obtained using hexane rather than cyclohexane as a countersolvent.
7. The settling rate of a system containing hexane is noticeably higher than that of a system containing cyclohexane
8. The settling rate of a system containing cyclohexane is more sensitive to an increase in water to solvent ratio than is a system containing hexane

It can therefore be concluded that high percentages of aniline in the feed stream cannot be removed effectively using the proposed solvent system. Very little improvement in the removal of aniline from the extract phase can be achieved by the manipulation of parameters such as impeller speed and increased residence time in the extraction column.

Variations in the hydrodynamic conditions in the extraction column can however influence the extent to which o-tolunitrile is removed. The removal of o-tolunitrile is therefore emphasised in further pilot plant tests

7.5.4 Results of second set of pilot plant runs

A further set of pilot plant tests were carried out on the synthetic feed stream in order to optimise the performance of the extraction column. These pilot plant tests differed most significantly from the preliminary tests with respect to the water to solvent and hexane to feed ratios employed as well as the flow rates of the streams entering the extraction column.

Lower water to solvent ratios than that used in the preliminary test were employed in order to enhance phase disengagement, settling efficiency and therefore stage efficiency. Thus, water to solvent ratios in the range 0.07 to 0.22, as opposed to 0.3 were used.

The flowrates of the combined feed and solvent stream as well as that of the hexane stream were substantially decreased. The total throughput of the column was therefore decreased and the retention time of the phases in the column consequently increased.

The flowrate of the hexane stream was adjusted according to the rotameter readings and calibration chart. The rotameter was originally calibrated for significantly higher flowrates, such as those used in the preliminary pilot plant test. The validity of the extrapolated calibration curve was therefore tested after the pilot plant runs were completed. It was found that the rotameter readings corresponded to higher hexane flow rates than was initially assumed. The hexane to feed ratios for the pilot plant tests are therefore higher than the optimum values determined for the batch extractions tests. The higher hexane to feed ratio does not however detract form the relevance of the results obtained from the pilot plant tests. The phenol and m-cresol synthetic streams used for the batch extractions, as well as a typical industrial feed stream, contain

significant percentages of neutral oils such as mesitylene, pseudocumene, undecane, dodecane, indene and indane. All of these components perform as countersolvents and are absent in the synthetic pilot plant feed stream. The higher hexane to feed ratio can therefore be regarded as a compensation for the absence of the neutral oils with countersolvent properties in the feed stream. Also, both the cresol and aniline concentrations in the synthetic pilot plant stream are significantly higher than those used in the batch extractions executed on the phenol and m-cresol feed streams. The hexane to cresol ratio, as well as the hexane to aniline ratio is therefore essentially lower in the pilot plant runs than in the batch extractions.

The shake-up tests showed that cyclohexane was a less effective countersolvent than hexane for the system under investigation. Three pilot plant tests were carried out using cyclohexane as countersolvent in order to ascertain whether the same was true for a multistage extraction process.

The results obtained from the pilot plant tests are given in Table 7-7. The results obtained from the preliminary pilot plant test, PP1, are included for comparison.

Table 7-7. Pilot plant test results: percentage recovery of m-cresol + p-cresol, R_{Cresol}, percentage of feed aniline $R_{Aniline}$ and o-tolunitrile $R_{o\text{-}Tolunitrile}$ remaining in the solvent phase and percentage purity of the cresol isomers with respect to aniline and o-tolunitrile in the extract phase, P_{Cresol} for various solvent to feed, hexane to feed and water to solvent mass ratios, total volumetric throughputs, Q_{total}, rotation speed of impellers, ω, and temperature at the midpoint of the extraction column, $T_{midpoint}$.

		Solvent Ratios			ω	$T_{midpoint}$	Q_{total}	$R_{Aniline}$	$R_{o\text{-}Tolunitrile}$	R_{Cresol}	P_{Cresol}
	countersolvent	S/F	H/F	W/S	rpm	[°C]	[l/h]	[%]	[%]	[%]	[%]
PP1	Hexane	2.6	5.3	0.31	260	36.5	59	79.7	10.9	94.7	90.9
PP2	Hexane	3.3	6.4	0.07	245	37.4	46	90.1	29.9	98.0	93.6
PP3	Hexane	3.3	6.5	0.07	235	34.2	35	90.1	31.7	97.9	93.2
PP4	Hexane	3.1	6.7	0.07	212	38.2	35	90.2	35.0	97.9	93.8
PP5	Hexane	3.1	7.9	0.07	320	37.3	39	88.1	24.0	97.8	94.2
PP6	Hexane	3.4	6.0	0.12	302	37.0	32	88.6	21.1	98.4	94.1
PP7	Cyclohexane	4.1	7.5	0.22	245	33.5	59	83.9	6.7	97.7	91.5
PP8	Cyclohexane	3.3	6.9	0.07	245	35.0	59	88.3	32.8	97.7	93.5
PP9	Cyclohexane	3.3	6.6	0.07	0	35.4	43	91.7	40.0	97.7	93.3

It is clear from Table 7-7 that, as was found with the hydrodynamic tests, the parameter that has the most significant effect on the removal of aniline and o-tolunitrile from the extract phase is the water to solvent ratio. At the low water to solvent ratio of 0.07, the percentage of feed o-tolunitrile remaining in the extract phase ranges from

approximately 30 to 35% for the tests using hexane as a countersolvent. The only pilot plant test executed with a water to solvent ratio of 0.07 that yielded an o-tolunitrile recovery significantly lower than 30% was executed at a significantly higher hexane to feed ratio (7.9 as opposed to approximately 6.5) and high impeller rotation speed (320 rpm as opposed to 212 to 245 rpm). Even at these favourable conditions, the o-tolunitrile recovery was 24.0%. The effect of the water to solvent ratio on aniline, although much less noticeable, is similar. The percentage of feed aniline remaining in the extract phase is approximately 90% for all pilot plant tests carried out with hexane to feed ratios of approximately 6.5 and water to solvent ratios of 0.07. A slight decrease in the aniline recovery, from approximately 90% to 88.1%, is obtained by increasing the hexane to feed ratio to 7.9 and increasing the impeller rotation rate to 320 rpm.

An increase in the water to solvent ratio from 0.07 to 0.12 and 0.31 clearly effects an improvement in both the aniline and o-tolunitrile removal from the extract phase. Thus, it can be seen that for test PP1, which was carried out at a water to solvent ratio of 0.3, both the percentage of feed aniline and o-tolunitrile remaining in the extract phase is substantially lower than those obtained for pilot plant tests carried out at lower water to solvent ratios. This is especially significant as the hexane to feed ratio employed in the first pilot plant test was significantly lower than those employed in subsequent tests.

This is confirmed by the results obtained for pilot plant tests PP5 and PP6. The solvent to feed ratio is lower, while the hexane to feed ratio is higher in PP5 than in PP6. Furthermore, the impeller speed in PP5 is higher than in PP6. I.e., apart from the water to solvent ratio, the conditions for the removal of o-tolunitrile are more favourable in PP5 than in PP6. Despite this fact, a relatively small increase in the water to solvent ratio from 0.07 to 0.12 results in a lower percentage of o-tolunitrile remaining in the extract phase.

The same trend is observed in the pilot plant tests carried out using cyclohexane as countersolvent. In tests PP7 and PP8, the impeller speeds are the same at 245 rpm, and the ratio of the hexane to feed ratio is approximately double that of the solvent to feed ratio. In PP7, however, the water to solvent ratio is significantly higher, at 0.22, than is the water to solvent ratio of 0.07 used for PP8. A substantially larger percentage of o-tolunitrile is consequently removed from the extract phase in PP7. The percentage of aniline remaining in the extract phase is also noticeably decreased at the higher water to solvent ratio.

It can further be seen from the results obtained for pilot plant tests PP4, PP3, PP2 and PP5 respectively, that an increase in the rotation speed of the impellers results in a decrease in the percentage of o-tolunitrile remaining in the extract phase. The impeller speed appears to have no discernible effect on aniline removal or the recovery of the cresol isomers.

The negligible effect of impeller speed on cresol recovery is confirmed by the results obtained for test PP9 in which the extraction column was operated as an unagitated sieve tray column. The cresol recovery obtained for test PP8, at an impeller speed of 245 rpm, is identical to that obtained for test PP9. The percentage of feed aniline and feed o-tolunitrile remaining in the extract phase are however noticeably higher in the unagitated test. It can therefore be concluded that the impeller speed can be increased to effect more efficient removal of o-toluntrile and, to a lesser extent, aniline from the extract phase, without any corresponding decrease in cresol recovery.

From Table 7-7 it can be seen that, for the same temperature, solvent ratios, shaking times and settling times, a similar removal of aniline and o-tolunitrile from the extract phase is achieved using cyclohexane and hexane. Tests PP2 and PP8 were carried out at approximately the same hexane to feed and cyclohexane to feed ratios respectively. The water to solvent ratio and rotation speed of the impellers were identical for the two tests. While the percentage of aniline remaining in the solvent phase was margianlly lower for the cyclohexane extraction, the percentage of o-tolunitrile remaining in the solvent phase was marginally higher. As can be seen from Table 7-3, these results correspond to those obtained in the batch extractions carried out with cyclohexane and hexane. It can also be seen that, as was the case with the batch extractions, the recovery of the cresol isomers achieved using cyclohexane as a countersolvent is lower than achieved with hexane.

The boiling points of hexane and cyclohexane are 68°C and 81°C respectively. The recovery of hexane as distillate from the neutral oils in the countersolvent recovery column is consequently easier than the corresponding recovery of cyclohexane. Also, as the volume of countersolvent required on industrial scale will be large, the additional energy costs required to heat cyclohexane, rather than hexane, to boiling point can be expected to be significant. As such, hexane is the preferred countersolvent.

Another factor to be taken into consideration in the pilot plant tests is the recovery of the cresol isomers. It can be seen from Table 7-7 that the recovery of the cresol isomers is excellent for the pilot plant runs carried out with both hexane and cyclohexane as countersolvent. At water to solvent ratios of 0.07 to 0.22, cresol recoveries in excess of 97.5% are achieved. The cresol recovery obtained for pilot plant test PP1, at a water to solvent ratio of 0.3, is very good at 94.7%. However, it must be kept in consideration that the recoveries of the xylenol isomers obtained in batch extraction tests were considerably lower than those obtained for the cresol isomers at corresponding solvent ratios. Also, the recovery of the xylenol isomers was determined to be extremely sensitive to an increase in the water to solvent ratio. As such, it is not advisable to use a water to solvent ratio higher than 0.2.

The conclusions drawn from the pilot plant tests carried out on the synthetic feed stream are therefore:

- Large amounts of aniline in the feed cannot be removed using the proposed solvent system
- Although total removal of o-tolunitrile is not achieved, a significant amount of feed o-tolunitrile is removed
- The percentage recovery of the cresol isomers is excellent
- An increase in the water to solvent ratio leads to a significant decrease in the percentage of feed o-tolunitrile remaining in the extract phase
- A significant increase in the water to solvent ratio is required to effect a decrease in the percentage of aniline remaining in the extract phase
- An increase in the water to solvent ratio to approximately 0.2 does not lead to any noticeable decrease in cresol recovery. A further increase in the water to solvent ratio results to 0.3 results in a decrease in the cresol recovery
- An increase in the impeller rotation speed over a range of 212 to 320 rpm results in better o-tolunitrile removal, but has a negligible effect on the aniline recovery and has no effect on the cresol recovery
- The percentage of aniline and o-tolunitrile remaining in the extract phase increases significantly if the extraction column is not agitated. The percentage of cresol remains unaffected.

It can thus be concluded that a water to solvent ratio of 0.2 is optimum for multistage extraction and that the impeller rotation speed should be as high as possible.

7.5.5 Effect of Temperature

A final factor to be taken into consideration is the effect of temperature on the removal of aniline and o-tolunitrile from the extract phase.

The effect of an increase in temperature from 40°C to 45°C on the feed component recovery and separation efficiency is shown in Table 7-8.

Table 7-8. Effect of increase of temperature from 40 °C to 45°C on component recovery and separation efficiency

Exp ID	Solvent Ratios			T	Percentage of Feed Components in Extract Phase [%]				Separation Factors	
	H/F	S/F	W/S	[°C]	$R_{aniline}$	$R_{o\text{-}tolu\text{-}nitrile}$	$R_{m\text{-}cresol}$	$R_{p\text{-}cresol}$	$\beta_{cresol,\ aniline}$	$\beta_{cresol,\ o\text{-}tolunitrile}$
PPB	5.0	3.1	0.12	45	91.9	57.3	97.2	98.3	3.9	32.3
Amp13	5.4	3.0	0.07	40	93.5	63.3	98.2	98.6	3.9	32.2
Amp14	5.5	3.0	0.13	40	91.3	55.3	97.8	98.4	4.3	36.5
Amp15	5.0	3.2	0.14	40	92.1	59.0	97.8	98.4	3.9	31.6

A comparison of the results obtained for batch extractions PPB and Amp15 show that an increase in temperature from 40°C to 45°C has little effect on the separation efficiency of the solvent system. There is no effect on the cresol-aniline separation factor, despite the slight decrease in the percentage of aniline remaining in the extract phase at the higher temperature. This can be attributed to the corresponding decrease in the percentage recovery of the cresol isomers. Similarly, the effect on the cresol-o-tolunitrile separation factor and percentage of o-tolunitrile remaining in the extract phase is slight. It can further be seen that small changes in the solvent ratios have a more significant effect on the separation efficiency than does an increase in the temperature.

From Table 7-7 it can be seen that, for pilot plant runs PP2 and PP3, the percentage of feed aniline remaining in the extract phase remains constant at 90.1% despite an increase in both the rotation speed of the impellers as well as the temperature. The temperature at the midpoint of the column for these two pilot plant tests differs by 3.2°C.

Despite the higher extractor temperature in pilot plant test PP2, no difference in the percentage recovery of aniline is obtained. The percentage recovery of o-tolunitrile is also only marginally lower, at 29.9%, for pilot plant test PP2 than it is, at 31.7%, for pilot plant test PP3. It has been concluded from the pilot plant test results that an increase in the rotation speed of the impellers results in a decrease in the percentage of feed o-tolunitrile remaining in the extract phase. The lower percentage recovery of o-tolunitrile in pilot plant test PP2 could therefore be attributed to the higher impeller rotation speed.

The results from pilot plant tests PP3 and PP4 should therefore be noted. The temperature at the midpoint of the column for pilot plant test PP4 is 4.0°C higher than that for pilot plant test PP3. Despite the fact that the system temperature is higher in PP4 than it is in PP3, the percentage recovery of aniline is marginally higher, at 90.2%,

in PP4 than it is, at 90.1%, in PP3. The percentage recovery of o-tolunitrile is also significanly higher at the higher extractor temperature, namely 35.0% at 38.2°C as opposed to 31.7% at 34.2°C. The higher recovery of aniline and o-tolunitrile can be attributed to the fact that the rotation speed of the impellers is signifcantly lower for pilot plant test PP4 than it is for PP3.

It must also be borne in mind that the conclusion drawn from the hydrodynamic tests was that the removal of aniline is limited by the affinity of aniline for triethylene glycol and not by hydrodynamic factors. An increase in temperature might well increase the rate at which mass transfer occurs, but there is no guarantee that the affinity of aniline for triethylene glycol will be significantly decreased. Furthermore, as both aniline and the phenolic compounds are held in the solvent phase by means of hydrogen bonding with the triethylene glycol molecule, a decrease in the affinity of aniline for triethylene glycol may well coincide with a decrease in the affinity of the phenolic compounds for triethylene glycol. I.e. an increase in temperature may well lead to a decrease in phenolic recovery. From Table 7-8 and a comparison of Table 7-1 and Table 7-2 it can be seen that the recovery of the cresol isomers does in fact decrease with an increase in temperature. .

Pilot plant tests were performed in industry as an extension of this study. In these pilot plant tests, the extractor temperature was increased to 55°C. No improvement in separation efficiency was obtained and occasionally vapour bubbles were observed in the extractor.

From the above it can be concluded that the effect of temperature on the removal of o-tolunitrile and aniline at temperatures in the range of 34 to 55°C is much less significant than the effect of parameters such as the solvent ratios and impeller rotation speed.

7.5.6 Simulation of Pilot plant tests

The pilot plant tests conducted with hexane as a countersolvent were simulated with the simulation package PROII version 5.1 (Simulation Sciences Inc.). The thermodynamic model used was the three parameter NRTL model discussed in Chapter 6. The binary parameters for the NRTL were those listed in Table 6-11, which were obtained by regression of the LLE data generated in batch extraction tests. A typical input file and excerpts from the corresponding output file are listed in Appendix D2.

The pilot plant column was simulated as a liquid-liquid extraction column consisting of a specified number of equilbrium stages. In simulating a pilot plant test, the composition, temperature and flowrates of the process streams entering the extraction column were specified as being the same as in the pilot plant test.

7.5.6.1 Equilibrium Stage Efficiency

The first purpose of simulating the pilot plant tests was to determine the number of theoretical equilibrium stages required to obtain the same percentage recovery of o-tolunitrile in the simulated extract phase as was experimentally obtained for each pilot plant test. If the simulations of the pilot runs yield satisfactory results, the model can be used with confidence in the conceptual design of a process.

An equilibrium stage-based simulator was used. In the simulation, the two feed streams are specified as being the same as used in the experimental run. The number of theoretical stages is then varied in the simulator until the simulated o-tolunitrile values in the extract and raffinate closely matches the experimental values. This fixes the number of theoretical stages in the column.

The pilot plant extraction column consists of 28 repetitive units, each of which consists of a mixing and settling zone. The number of these repetitive units that correspond to a single theoretical equilibrium stage can therefore be calculated as the total number of repetitive units divided by the number of theoretical equilibrium stages as determined by means of simulation.

The average stage efficiency of a repetitive unit in the pilot plant extraction column can consequently be calculated as:

$$\eta = 100 / (28 / N_T) \quad [\%] \qquad (7.5\text{-}3)$$

where

η : equilibrium stage efficiency of a single repetitive unit
N_T : number of theoretical equilibrium stages

It should however be borne in mind that, as in other unit operations such as distillation, the stage efficiency does not have to be the same for all components. The average stage efficiency as defined above is thus, srictly speaking, based on o-tolunitrile.

The number of theoretical equilibrium stages required to obtain the same percentage of feed o-tolunitrile remaining in the extract phase for each pilot plant test can similarly determined for each of the pilot plant tests. The percentages of each feed component remaining in the extract phase for successive simulated number of theoretical stages are listed in Table 7-9 along with the percentage of the feed components remaining in the extract phase after each pilot plant test.

Table 7-9. Experimental and corresponding simulated percentages of feed aniline, o-tolunitrile, m-cresol and p-cresol remaining in the extract phase after multistage countercurrent extraction.

Pilot Plant Test	Feed Component	EXPERI-MENTAL RESULTs	SIMULATION RESULTS					
			Number of Stages in Simulated Extraction Column					
			1	2	3	4	5	6
		Percentage of Feed Component Remaining in Extract Phase						
PP1	Aniline	**79.7**	85.8	84.0	83.7	83.6	**83.6**	83.6
PP1	o-Tolunitrile	**10.9**	44.1	26.2	17.5	12.4	**9.1**	6.8
PP1	m-Cresol	**96.7**	96.7	96.7	96.6	96.6	**96.6**	96.6
PP1	p-Cresol	**96.1**	96.2	96.1	96.1	96.0	**96.0**	96.0
PP2	Aniline	**90.1**	92.8	92.3	92.3	92.3	92.3	**92.3**
PP2	o-Tolunitrile	**29.9**	57.2	43.8	37.4	33.8	31.6	**30.2**
PP2	m-Cresol	**98.0**	98.6	98.6	98.6	98.6	98.6	**98.6**
PP2	p-Cresol	**98.0**	97.2	97.2	97.2	97.2	97.2	**97.2**
PP3	Aniline	**90.1**	92.1	91.6	91.5	**91.5**	91.5	91.5
PP3	o-Tolunitrile	**31.7**	54.8	40.3	33.0	**28.8**	26.0	24.2
PP3	m-Cresol	**97.9**	98.4	98.4	98.4	**98.4**	98.4	98.4
PP3	p-Cresol	**97.9**	96.9	96.9	96.9	**96.9**	96.9	96.9
PP4	Aniline	**90.2**	91.5	90.8	**90.8**	90.8	-	-
PP4	o-Tolunitrile	**35.0**	53.7	38.7	**31.3**	26.9	-	-
PP4	m-Cresol	**97.9**	98.3	98.3	**98.3**	98.3	-	-
PP4	p-Cresol	**97.9**	96.9	96.9	**96.9**	96.9	-	-
PP5	Aniline	**88.1**	91.4	90.8	90.7	90.7	**90.7**	90.7
PP5	o-Tolunitrile	**24.0**	53.7	38.7	31.1	26.7	**23.7**	21.7
PP5	m-Cresol	**97.8**	98.3	98.3	98.3	98.3	**98.3**	98.3
PP5	p-Cresol	**97.8**	96.9	96.9	96.9	96.9	**96.9**	96.9
PP6	Aniline	**88.6**	90.9	90.1	90.1	90.1	**90.1**	-
PP6	o-Tolunitrile	**21.1**	52.3	36.7	28.8	24.1	**21.0**	-
PP6	m-Cresol	**98.4**	98.2	98.1	98.1	98.1	**98.1**	-
PP6	p-Cresol	**98.4**	97.0	97.0	97.0	97.0	**97.0**	-

It can be seen from Table 7-9 that little or no decrease in the percentage of feed aniline, m-cresol and p-cresol remaining in the extract phase after a single theoretical equilibrium separation stage can be obtained with the addition of extra equilibrium stages.

Only the percentage of feed o-tolunitrile remaining in the extract phase decreases with an increase in the number of theoretical equilbrium separation stages. It is for this reason that the feed percentage of o-tolunitrile remaining in the extract phase was selected as the basis for the determination of the number of theoretical equilibrium stages.

The number of theoretical equilibrium stages and equilibrium stage efficiency of the extraction column are given in Table 7-10 for each of the pilot plant tests carried out with hexane as a countersolvent.

Table 7-10. Number of theoretical stages, N_T, and stage efficiencies, η, for the pilot plant extraction column at various impeller rotation speeds, ω, and solvent to feed (S/F), hexane to feed (H/F) and water to solvent (W/S) mass ratios.

	S/F	H/F	W/S	ω [rpm]	N_T	η [%]
PP1	2.6	5.3	0.31	260	5	17.9
PP2	3.3	6.4	0.07	245	6	21.4
PP3	3.3	6.5	0.07	235	4	14.3
PP4	3.1	6.7	0.07	212	3	10.7
PP5	3.1	7.9	0.07	320	5	17.9
PP6	3.4	6.0	0.12	302	5	17.9

It can be seen from Table 7-10 that the equilibrium stage efficiency of the pilot plant extraction column, at approximately 10-20%, is considerably lower than the 25-55% stage efficiency predicted by Figure 7.2-2 for a standard Kühni column with a corresponding stator plate free cross-sectional area. This is despite the fact that the total column throughputs used in the pilot plant tests were considerably lower than those illustrated in Figure 7.2-2 and that additional stator plates and wire mesh packing were inserted between the mixing stages of the pilot plant column.

It can further be seen from Table 7-10 that low impeller rotation speed and high water to solvent ratios result in low stage efficiency. E.g., although the impeller rotation speed in pilot plant test PP1 is relatively high at 260 rpm, the high water to solvent ratio of 0.3 causes the stage efficiency to be lower than that of PP2 which is carried out a lower impeller speed. On the other hand, a comparison of tests PP5 and PP6 show that the negative effect on the stage efficiency of an increase in the water to solvent ratio from 0.07 to 0.12 is counteracted by the corresponding increase in impeller rotation speed. from 302 to 320 rpm. It can therefore be concluded that high water to solvent ratios should not be used in conjunction with low impeller rotation speeds.

Figure 7.2-2 shows that the stage efficiency of a Kühni column is higher at lower column throughputs. This is due to the fact that lower column throughputs result in longer retention times. I.e. the two liquid phases have more time to reach equilibrium in the extraction column. However, at low column throughputs the settling velocity of the heavy dispersed phase droplets through the continuous hexane phase limits the retention time of the heavy dispersed phase in the extraction column. A further reduction in the column throughput will therefore not lead to a significant increase in stage efficiency. Only more vigorous agitation can lead to smaller droplets, lower settling velocities and thus longer retention times.

It can be therefore be concluded that, for the process under investigation, the stage efficiency of the extraction column is dependent on the extraction system. A mixer-settler extractor arrangement might therefore be considered to be more appropriate for the proposed extraction system. However, as can be seen Table 7-9, with the exception of the pilot plant test PP1, which was carried out at a high water to solvent ratio of 0.3, no additional removal of aniline is achieved with the addition of separation stages. It is therefore clear that a pinch concentration of aniline in the extract phase exists. Under these circumstances, further removal of aniline can only be achieved by changing the operating line of the extraction column by contacting the extract phase with pure hexane. The separation of aniline from phenolic compounds achieved in a mixer settler arrangement is therefore not expected to be noticeably better than that achieved in the extraction column.

7.5.6.2 Optimum position of feed point

A further purpose of simulating the pilot plant system was to determine the optimum point at which the feed stream should enter the extraction column. An extraction column consisting of five theoretical stages was simulated for the solvent, water, feed

and hexane flowrates corresponding to pilot plant test PP6. The stage at which the feed stream entered the column was varied. The simulated percentages of the feed components remaining in the extract as well as those experimentally determined for pilot plant test PP6 are shown in Table 7-11.

Table 7-11. Effect of feed entry point on percentage of feed components remaining in the extract phase.

	Pilot Plant	Simulation Results		
Component	Number of theoretical separation stages from the top of the column at which feed enters.			
	0	0	1	2
	Percentage of Feed Component Remaining in Extract Phase			
Aniline	88.6	90.1	98.7	99.8
o-Tolunitrile	21.1	21.0	32.2	40.3
m-Cresol	98.4	98.1	100.0	100.0
p-Cresol	98.4	97.0	99.8	100.0

It is clear from Table 7-11 that the optimum point for the feed to enter the extraction column is at the top with the solvent stream. The percentage of feed aniline and o-tolunitrile increase significantly as the distance between the feed point and the top of the column increases. This can be attributed to the fact that the higher the point at which the feed components enter the column, the longer the flow path that they must follow before exiting the column. I.e. the exposure of the feed components to the hexane phase increases and, consequently, the potential for the transfer from the extract to the hexane phase increases.

It can therefore be concluded from the pilot plant tests carried out on the synthetic feed stream as well as from simulation results, that the optimum separation efficiency in the pilot plant column is achieved at a water to solvent ratio of approximately 0.2 combined with a high impeller rotation speed, using hexane as countersolvent. The feed stream should enter the extraction column at the top along with the solvent stream.

7.6 Industrial Feed Stream

The proposed separation process for the separation of phenolic compounds from neutral oils and nitrogen bases must ultimately be applied to industrial feed streams. A pilot plant test was therefore carried out on a typical industrial heavy naphtha stream

produced as a by-product of the pressure gasification of coal by means of the Lurgi process.

For the proposed solvent system to be considered successful, the final phenolic product purity after solvent recovery has to be within commercial specifications, i.e. greater than 99.5% by mass. A phenolic recovery greater than 90% is required for the proposed separation process to be feasible.

7.6.1 Analysis

The number of components in the industrial feed stream and the small differences in the boiling points of many of the components are such that analysis of the feed stream by means of gas chromatography is not feasible. The evaluation of the pilot plant performance is based on the percentage purity of the phenolic product as well as the recovery of the phenolic compounds in the feed. Therefore, while it is necessary to determine the relative concentrations of the combined phenolic compounds and combined neutral oils and nitrogen bases in feed, extract and raffinate streams, a quantitative analysis of the individual neutral oils, nitrogen bases and phenolic compounds is not required. All the impurities are therefore lumped in the analyses.

The feed and raffinate streams were therefore analysed by means of wet chemical analysis. The wet chemical analysis method used was one typically applied in industry and is based on the fact that the phenolic compounds react with sodium hydroxide to form water soluble sodium salts, while the nitrogen bases and neutral oils do not.

A schematic diagram of the wet chemical analysis procedure for the determination of the neutral oil and nitrogen base content of a sample is shown in Figure 7.5-1.

The first step in the analysis of the raffinate sample was the removal by distillation of the hexane from the phenolic compounds, neutral oils and nitrogen bases in the sample. This step was not required for the feed sample. The subsequent analysis procedure was identical for both the residual raffinate and feed samples.

The mass of the phenolic compounds present in the sample to be analysed was estimated. An excess, ten times the stoichiometric amount required, of sodium hydroxide was added as an aqueous solution to the sample to be analysed. The reaction mixture was heated in a flat-bottomed glass flask attached to a Liebig condenser, while being stirred continuously with a magnetic stirrer. As the reaction mixture heated, the phenolic compounds reacted to form water-soluble sodium salts (Step 1. in Figure 7.5-1).

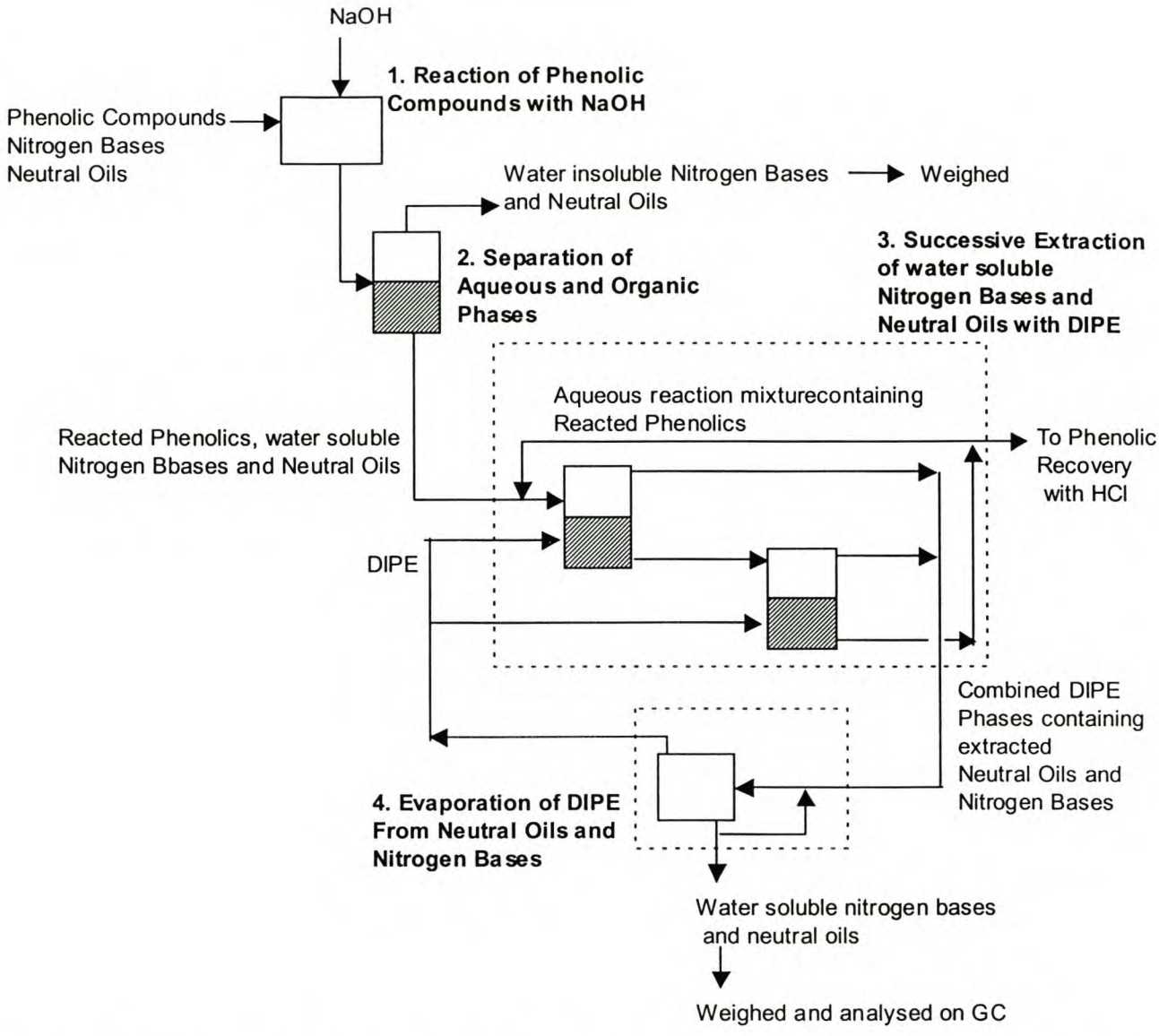


Figure 7.6-1 Schematic diagram of the wet chemical analysis procedure for the determination of the neutral oil and nitrogen base content of a sample

The bulk of the unreacted nitrogen bases and neutral oils formed an immiscible organic layer on the surface of the reaction mixture. The reaction mixture was cooled to ambient temperature and the two liquid phases were separated using a glass separating funnel (Step 2. in Figure 7.5-1). The aqueous phase containing the reacted phenolic compounds was then successively contacted with two equal volumes of di-isopropyl ether (DIPE) in order to extract any water-soluble neutral oils and nitrogen bases remaining in the aqueous phase (Step 3. in Figure 7.5-1). The DIPE phases resulting from the successive extraction steps were combined and the DIPE evaporated under vacuum from the neutral oils using a standard Rotavap apparatus, at a

temperature of approximately 50°C (Step 4. in Figure 7.5-1). The evaporated DIPE was recovered, divided into two equal volumes and each volume was contacted with the aqueous phase again. The resulting DIPE phases were added to the residual neutral oils recovered in the evaporation step and were then once again evaporated under vacuum from the neutral oils. The process was repeated until no further neutral oils were recovered in the evaporation step. The extracted neutral oils were then weighed and analysed by means of gas chromatography to ascertain that no unreacted phenolic compounds were present in the neutral oils. The analysis method used was the same as that used for the analysis of the extract phase and is discussed later. It was found in all cases that, despite the large excess of sodium hydroxide in the initial analysis step, a significant percentage of the neutral oil sample consisted of unreacted phenolic compounds. The water-insoluble and water-soluble neutral oils and nitrogen bases could thus be isolated and the mass thereof determined. The mass of phenolic compounds recovered with the neutral oils and nitrogen bases could be determined from the GC analyses.

The recovery of the phenolic compounds from the aqeuous reaction mixture is analogous to the recovery of the neutral oils and nitrogen bases. After removal of the residual neutral oils and nitrogen bases in the aqueous phase, an aqueous solution of hydrochloric acid (28% hydrochloric acid by mass) was added to reverse the original reaction and liberate the phenolic compounds. A 20% excess of the hydrochloric acid stoichiometrically required was used. The water-insoluble phenolic compounds formed an immiscible oily layer on the surface of the aqueous solution. The phenolic compounds were extracted from the aqueous solution by means of DIPE and the DIPE recovered using the same procedure as was used for the recovery of the netural oils. The resulting phenolic compound sample was then weighed and analysed on an HP 5890A GC-MS in order to ascertain that no neutral oils or nitrogen bases remained in the phenolic product. It was found that the phenolic product resulting from the wet chemical analysis technique contained no neutral oils.

Detailed calculations and results for the analysis of the feed and raffinate streams are given in Appendix F.

The phenolic content of the extract phase could not accurately be determined by means of wet chemical analysis due to the presence of triethylene glycol in the sample. While the triethylene glycol remains unreacted after treatment with sodium hydroxide, it does react to a limited degree with hydrochloric acid. Although only a very small percentage of the triethylene glycol reacts, it is sufficient to hinder the accurate determination of the concentration of phenolic compounds in the sample. Also, the triethylene glycol is miscible in DIPE and is therefore extracted from the aqueous phase with the neutral oils, nitrogen bases and phenolic compounds. The nitrogen bases and neutral oils must therefore first be removed from the reaction mixture containing the triethylene glycol by

means of azeotropic distillation with water. A large amount of water is required to ensure that all the neutral oils and nitrogen bases are removed as distillate. The volume of water to be contacted with DIPE in order to extract any water-soluble neutral oils is therefore large, and the concentration of the neutral oils contained therein is consequently very small. It can therefore not be ensured that all the neutral oils in the extract phase are accounted for in wet chemical analysis.

As the extract phase contains very few neutral oils and nitrogen bases, the analysis thereof by mean of gas chromatography is feasible. The extract phase was therefore analysed by means of gas chromatography using a Hewlett-Packard 5890A gas chromatograph with a flame ionisation detector. Integration was performed with computerized integration software. A 60 m Zebron D68H5 capillary column (inner diameter 0.25 mm) was used. In this column, the interaction of the neutral oils, nitrogen bases and phenolic compounds with the stationary phase is such that the bulk of the neutral oils and nitrogen bases have significantly lower retention times than do the phenolic compounds. I.e. the combined neutral oils and nitrogen bases appear as a group of peaks separate to those of the combined phenolic compounds. The neutral oils that do have retention times overlapping those of the phenolic compounds, such as the naphthalenes, are almost without exception removed from the extract phase during the multistage extraction process. It was found that o-toluidine is the only nitrogen base and remaining in the extract phase that has a retention time comparable to that of the phenolic compounds. I.e. all the component peaks appearing after a certain retention time could with confidence be assumed to be phenolic compounds, with the exception of o-toluidine which could easily be identified according to retention time and relative position to phenol.

The retention times for the various feed components were determined using an HP 5890 gas chromatograph attached to a mass spectrometer (GC-MS) and software including an extensive component identification database. The column used for the quantitative analyses was installed in the GC-MS. The identity and retention times of the components in the industrial feed streams for a given temperature program and carrier gas flow rate were ascertained for the column. The column was then installed in a standard GC with FID detector and the extract phase sample was analysed using the same temperature program as was used for the GC-MS analyses. As the temperature program and column used in the standard GC analyses were the same as those used in the GC-MS analyses, the order in which the components appeared on the chromatogram remained the same. I.e. the components in the extract phase sample could be identified and quantitatively analysed.

The neutral oils with retention times overlapping those of the phenolic compounds are present in the feed and raffinate samples. These could therefore not be analysed on the GC. It was ascertained using the GC-MS that the retention times of the water-

soluble neutral oils extracted with DIPE from the aqueous reaction mixture in the wet chemical analysis did not overlap those of the phenolic compounds. The phenolic compounds in the water soluble neutral oil sample could therefore be identified and consequently, the concentration of phenolic compounds in the sample could be determined.

7.6.2 Pilot plant setup

The pilot plant setup for the test carried out on the industrial feed stream differed from that used for the synthetic feed stream in only one respect. Due to the high percentage of triethylene glycol insoluble neutral oils in the industrial feed stream, the feed stream was not homogenous with the solvent stream. The feed and solvent streams were therefore pumped separately to the extraction column. The modified flow diagram is shown in Figure 7.6-2

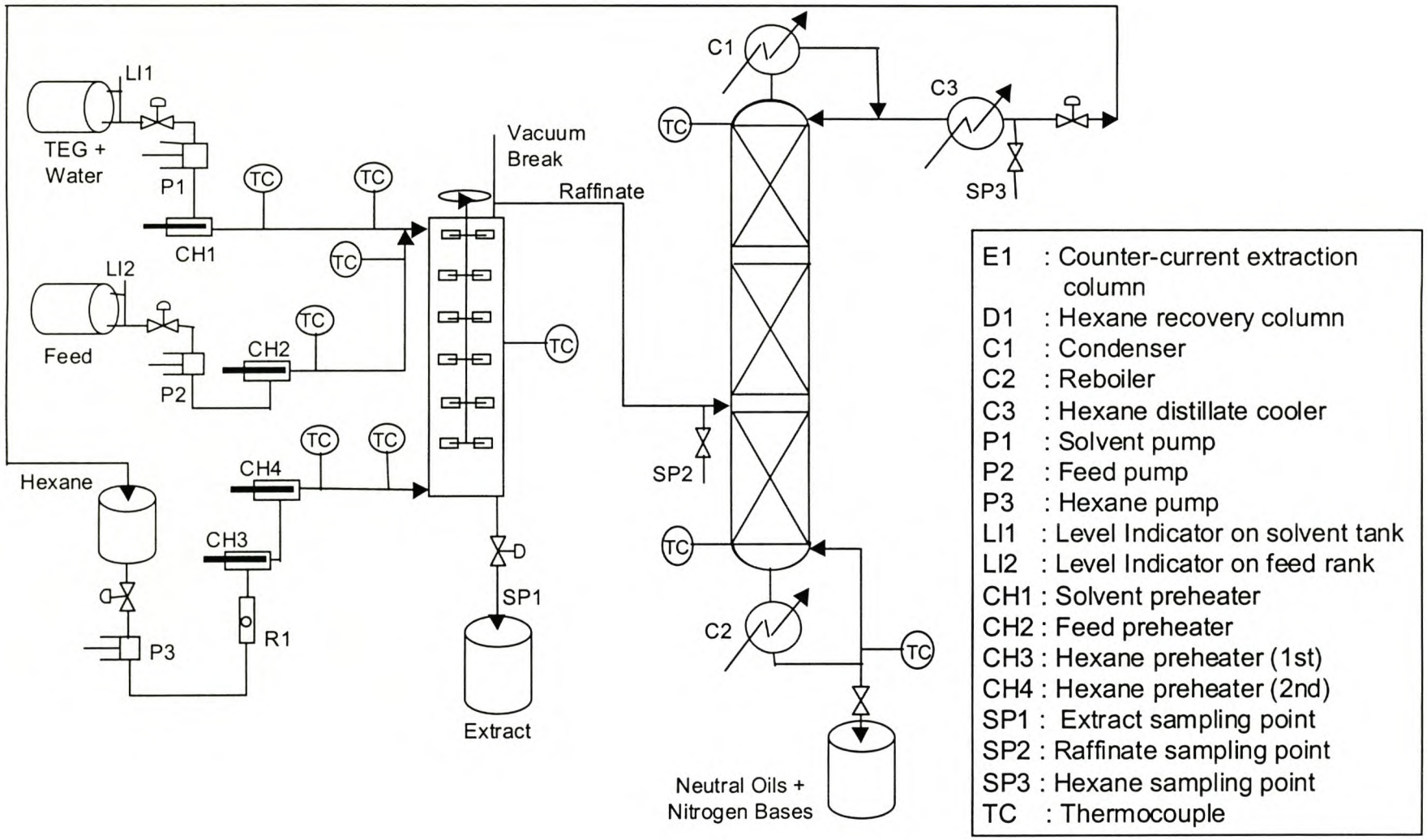


Figure 7.6-2. Process flow diagram of experimental setup for pilot plant tests using the industrial feed stream

7.6.3 Feed Stream

Table 7-12 lists the most prevalent components identified qualitatively in the heavy naphtha stream.

Table 7-12. Selected phenolic compounds, neutral oils and nitrogen bases present in the heavy naphtha stream used for pilot plant tests.

Phenolic Compounds	Nitrogen Bases	Neutral Oils
Phenol	Methylpyridine isomers	Dimethylbenzene isomers
o-Cresol	Dimethylpyridine isomers	Et-me-benzene isomers
m-Cresol	Trimethylpyridine isomers	Diethylbenzene isomers
p-Cresol	Et-me-pyridine isomers	Et-dime-benzene isomers
2,6-Xylenol	Aniline	2-Propyl-benzene
2,4-Xylenol	o-Toluidine	Tetramethylbenzene
2,5-Xylenol	m-Toluidine	Pseudocumene
2,3-Xylenol	p-Toluidine	Mesitylene
3,4-Xylenol		1,2,4-Trimethylbenzene
3,5-Xylenol		Indane
o-,m-and p-Ethyl-Phenol		Methylindane
C3-Phenols		Ethylindane
Trimethyl Phenols		Trimethylindane
Et-me-Phenols		Indene
		Methylindene
		Undecene
		Undecane
		Dodecane
		Naphthalene
		Benzofuran
		Benzonitrile
		o-Tolunitrile
		m-Tolunitrile
		p-Tolunitrile

7.6.4 Procedure

Based on the results obtained from the pilot plant tests performed on the synthetic feed stream, a relatively high water to solvent ratio of 0.25 was used in conjunction with a high impeller rotation speed of 320 rpm. The temperature of the feed, solvent and hexane streams entering the column was increased to ensure that a temperature of approximately 40°C was maintained in the extraction column.

The flowrates of the feed, solvent and hexane streams were measured with a calibrated measuring cylinder and stopwatch to ensure that the correct solvent ratios were maintained.

It was determined from the pilot plant tests on the synthetic feed stream that the number of theoretical stages in the extraction column is very low. In order to investigate the effect of additional theoretical stages on separation efficiency, the extract from the first pilot plant test on the industrial feed stream was collected and used as the combined solvent and feed stream for a second pilot plant test. Regenerated hexane was used in the second extraction.

The extract phase and raffinate phase were sampled after each pass through the extraction column.

A sample of the extract phase from the second pilot plant test was used in a separate water recovery step. The water recovery step was on a smaller scale than the countercurrent extraction process and was operated as a batch distillation in a 50 mm glass distillation column packed with random gauze packing. The volume of the extract phase sample used in water recovery was approximately 2.5 litres. The water was recovered as distillate at a temperature of 70°C and pressure of approximately 20 kPa.

The water-free extract was analysed as the final product, i.e. the phenolic compounds were not separated from the triethylene glycol.

The operating conditions applicable to the first pass of the industrial feed stream through the extraction column were as follows:

- Mass composition of feed: 49.9% phenolic compounds; 51.1% combined neutral oils and nitrogen bases
- Solvent to feed mass ratio: 3.0
- Hexane to feed mass ratio: 4.8
- Water to solvent mass ratio: 0.25
- Feed entry point at the top of the extraction column with the solvent stream

- Solvent stream temperature before entering column: 40.6°C
- Feed stream temperature before entering column: 39.4°C
- Hexane temperature before entering column: 43.0°C
- Rotation speed of impellers: 320 rpm
- Total volumetric throughput of both liquid phases: 55 litres per hour

The operating conditions for the second pilot plant test were identical to those for the first test, apart from the feed and solvent streams, which were replaced by the extract phase resulting from the first test.

The flow rates of the various process streams are shown in a schematic flow diagram of the two pilot plant tests combined in Figure 7.6-3.

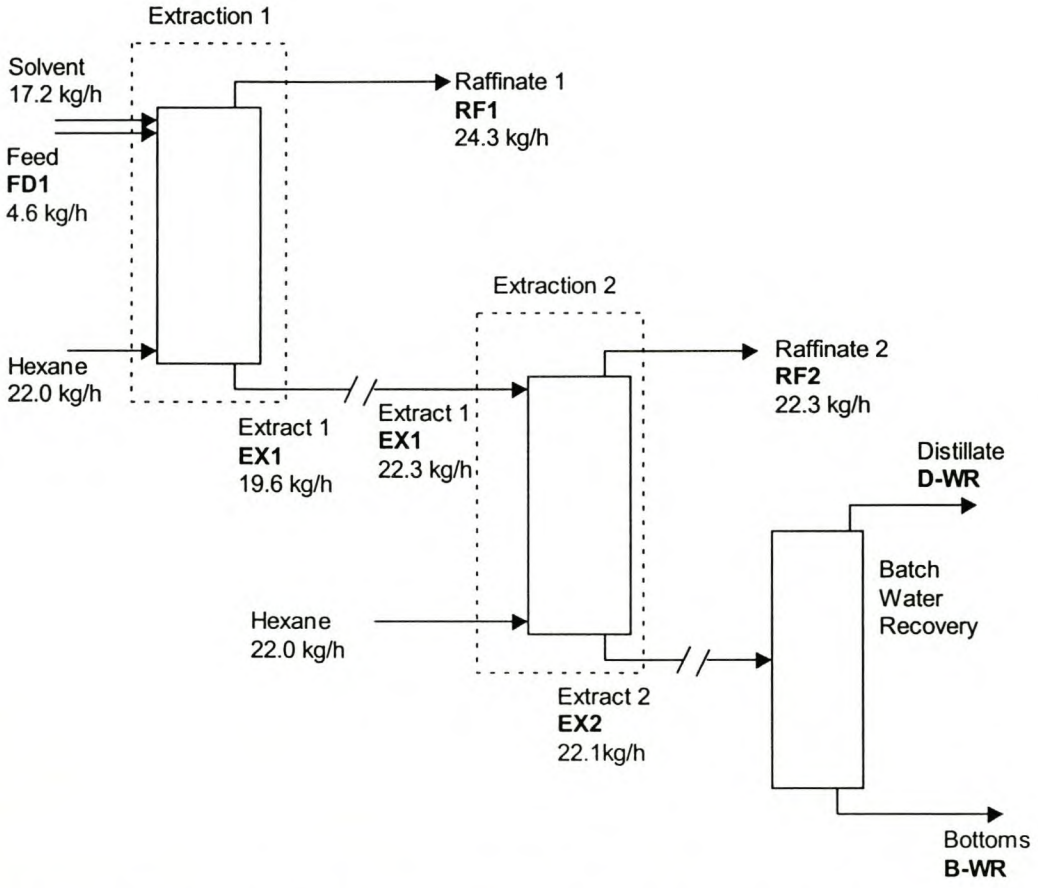


Figure 7.6-3 Schematic flow diagram of pilot plant tests on industrial feed stream.

7.6.5 Results

The percentage compositions of the various process streams shown in Figure 7.6-3 are listed in Table 7-13. The corresponding mass flowrates are listed in Table 7-14.

Table 7-13. Mass percentage compositions of pilot plant process streams

	Solvent	FD1	EX1	RF1	EX2	RF2	D-WR	B-WR
Hexane	0.0	0.0	0.20	89.37	0.20	99.72	1.0	0.00
Water	20.0	0.0	18.30	0.03	19.10	0.00	97.8	1.70
TEG	80.0	0.0	70.16	0.00	69.70	0.00	0.0	85.0
Phenolics	0.0	49.9	11.10	9.90	10.90	0.10	1.0	13.27
Neutral Oils + Nitrogen Bases	0.0	51.1	0.24	0.70	0.20	0.18	0.2	0.03

Table 7-14 Mass flowrates [kg/h] of pilot plant process streams

	Solvent	FD1	EX1	RF1	EX2	RF2
Hexane	0.00	0.00	0.04	21.66	0.04	22.22
Water	3.43	0.00	3.58	0.01	4.22	0.00
TEG	13.77	0.00	13.72	0.00	15.38	0.00
Phenolics	0.00	2.29	2.17	0.18	2.41	0.04
Neutral Oils + Nitrogen Bases	0.00	2.31	0.04	2.40	0.046	0.04
TOTAL	17.20	4.60	19.55	24.25	22.1	22.3

A mass balance over the components entering and exiting the extraction column was calculated for each pilot plant test in order to confirm the accuracy of the analysis results. The percentage error in the mass balances over the individual components for the two pilot plant tests are listed in Table 7-15.

It can be concluded from Table 7-15 that the accuracy of the analyses are satisfactory. The large percentage error obtained for the mass balance over the combined nitrogen bases and neutral oils for the second pilot plant extraction can be attributed to the very small concentration of these components in the extraction system.

Table 7-15. Component mass balance percentage errors, ε, over pilot plant extractions

Component	$\varepsilon_{Extraction\ 1}$ [%]	$\varepsilon_{Extraction\ 2}$ [%]
Hexane	-1.3	0.8
Water	4.6	3.2
TEG	-0.4	-1.8
Phenolics	2.3	-1.3
Neutral Oils + Nitrogen Bases	5.8	21.0

The phenolic product purities relative to neutral oils and nitrogen bases in selected process streams as well as the phenolic recoveries after each process step are listed in Table 7-16.

Table 7-16. Phenolic product purities relative to neutral oils and nitrogen bases and percentage recovery of phenolic compounds.

Process Stream	Phenolic Purity [%]
Extract after first multistage extraction	97.89
Extract after second multistage extraction	98.09
Bottoms of water recovery	99.76
Phenolic Recovery [%]	
First extraction process	94.4
Second extraction process	96.9
Water recovery process	99.7
Combined extraction processes	91.4
Combined extraction processes and water recovery	91.1

It can be seen from Table 7-16 that the phenolic product purity with respect to nitrogen bases and neutral oils achieved after water recovery is excellent, and in excess of the specified product purity. Analysis showed that the only neutral oils remaining in the extract phase after the first extraction step were benzonitrile and o-tolunitrile. The amount of o-tolunitrile relative to benzonitrile remaining was negligible. The nitrogen bases remaining in the extract phase were methylpyridine isomers, aniline and o-toluidine. Aniline accounted for approximately 40% and benzonitrile, o-toluidine and the combined methylpyridine isomers for approximately 30%, 20% and 10% respectively of the remaining nitrogen bases and neutral oils.

The phenolic recovery achieved after the first extraction process is very good, especially as the phenolic product contains many higher substituted phenolic compounds which are not successfully recovered by the alternative processes discussed in Chapter 2.

It can further be seen that the purity of the phenolic product is significantly increased in the water recovery process. All the methylpyridine isomers, benzonitrile and o-tolunitrile was removed from the extract phase. The residual concentration of aniline and o-toluidine in the extract phase was also significantly decreased.

While the percentage of residual nitrogen bases and neural oils in the extract are substantially decreased during the water recovery process, the corresponding decrease in phenolic recovery is negligible. It can therefore be concluded that the hydrogen bonds formed between the phenolic compounds and triethylene glycol are strong enough that the phenolic compounds are not lost in the distillate along with the neutral oils and nitrogen bases.

It is also clear from Table 7-16 that a negligible increase in phenolic product purity is achieved by the additional extraction process performed on the extract phase of the first extraction. This can be expected as aniline and o-toluidine make up the bulk of the residual nitrogen bases and neutral oils in the extract phase after the first extraction. Simulation results have shown that the percentage recovery of aniline does not decrease with additional separation stages. It can be expected that the removal of o-toluidine will be similarly limited. Analyses show that the composition of the residual neutral oils and nitrogen bases in the extract of the second extract phase is in fact very similar to that in the first. I.e. the decrease in the residual pyridine and benzonitrile concentration is also negligible.

A significant decrease in phenolic recovery is however obtained. As the difference in the purities obtained after one and two extraction processes respectively is so small, it can be concluded that the increase in purity effected by the water recovery process will be sufficient to achieve a final phenolic purity of greater than 99.5% for a single extraction process. The second extraction is therefore not justified.

It can finally be concluded from the pilot plant results listed in Table 7-16 that a phenolic product purity in excess of the required purity of 99.5% with respect to neutral oils and nitrogen bases can be achieved for a typical industrial feed stream, using the proposed solvent system, despite the low stage efficiency of the extraction column used. A recovery of phenolic compounds in excess of 91% can be obtained simultaneously.

Based on the results obtained from the pilot plant test on the industrial feed stream, industry considered further investigation of the proposed separation process justifiable.

The first step in this development has already commenced. The entire process, including all the recovery columns, is being run continuously for a period of six weeks. The first results are extremely promising, verifying the results of this study. Due to the commercially sensitive nature of this information, industry has chosen to classify it as strictly confidential.

CHAPTER 8. CONCEPTUAL PROCESS DESIGN

It has been verified on pilot plant scale that the proposed solvent system is effective for the separation of phenolic compounds from neutral oils and nitrogen bases in a multistage extraction column. However, only a section of the proposed separation process was operated continuously. The phenolic compounds were not recovered from the triethylene glycol and the water and triethylene glycol recovery steps were not operated continuously. The phenolic product purity was calculated relative to the neutral oils and nitrogen bases in the extract phase only, i.e. it was assumed that no residue of the solvents, hexane, water and triethylene glycol would remain in the phenolic product after solvent recovery. Similarly, in calculating the phenolic recovery, it was assumed that all the phenolic compounds could be recovered from the triethylene glycol. The validity of these assumptions, as well as factors such as solvent losses and the influence of residual neutral oils and nitrogen bases in the recycled solvent phase on separation efficiency can only be investigated if the entire process, including all the solvent recovery steps are operated continuously.

Other factors that are critical in evaluating the commercial viability of the process include the size of the process equipment required as well as the energy and utility usage of each process step. Another critical factor to be investigated is the operating conditions required for the removal of the phenolic compounds from the triethylene glycol. Triethylene glycol is prone to thermal decomposition at temperatures above 210°C. It is therefore of paramount importance to ascertain whether the temperature in the reboiler of the column in which the triethylene glycol and phenolic compounds are separated exceeds 210°C.

A comprehensive overview of the process, including the solvent recovery steps that were not investigated in the pilot plant tests is clearly required. Therefore, the entire proposed separation process was simulated with ProII, version 5.1.

8.1 Flow sheet

The block flow diagram of the proposed process was given in Chapter 7. A more detailed process flow diagram of the process as it is expected to be implemented in industry is shown in Figure 8.1-1.

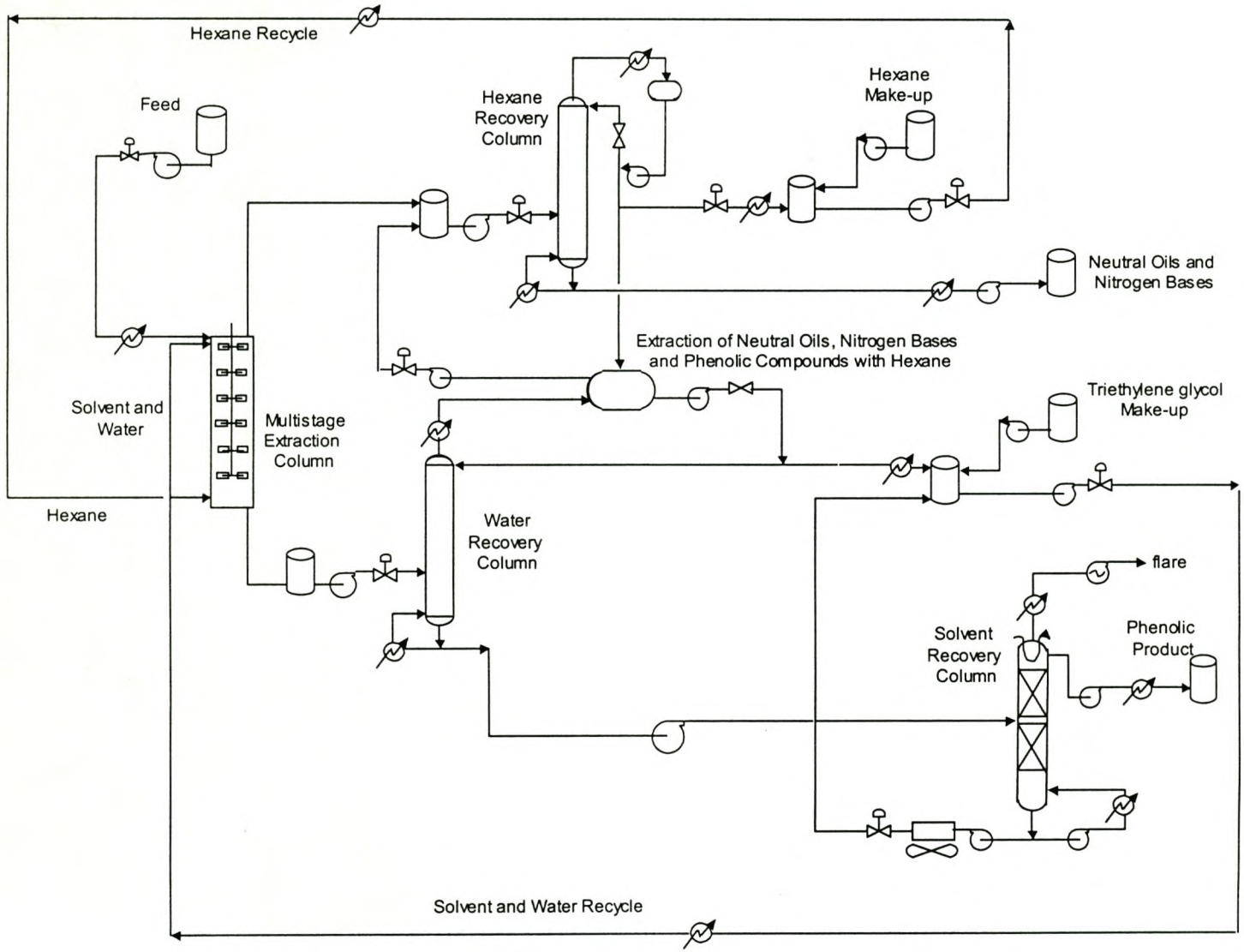


Figure 8.1-1. Process Flow Diagram for Proposed Process

8.2 Process Description

The feed stream to the extraction column consists of a mixture of phenolic compounds, neutral oils and nitrogen bases. The solvent stream, consisting of triethylene glycol and water, enters the extraction column at the top along with the feed stream, while the countersolvent stream, consisting of hexane, enters the extraction column at the bottom. The hexane phase is the light continuous phase and moves upwards through the column while the solvent phase is the heavy dispersed phase and moves downwards. The components of the feed stream are distributed between the two phases by means of countercurrent extraction. The resulting raffinate and extract phases exit the top and bottom of the column respectively.

The countersolvent phase exiting the extraction column consists of hexane, the neutral oils and nitrogen bases as well as traces of the phenolic compounds, water and triethylene glycol. It is fed to the hexane recovery column. In this column, the hexane (bp. 68°C) and any water present (bp. 100°C) are removed as the overhead product stream and recycled to the extraction column. The neutral oils, nitrogen bases, phenolic compounds and triethylene glycol in the raffinate all have boiling points in excess of 180°C. Hexane with a high purity with respect to neutral oils and nitrogen bases can therefore easily be recovered. It is unnecessary to remove any residual water in the hexane distillate as both the hexane and water in the process cycle are ultimately recycled to the extraction column. A small fraction of the hexane distillate is drawn off and used to extract organic compounds from the distillate from the water recovery column before being recycled to the hexane recovery column. This operation will be discussed in more detail subsequently.

The solvent phase leaving the extraction column consists of triethylene glycol, water, the bulk of the phenolic compounds in the original feed mixture and traces of neutral oils, nitrogen bases and hexane. It is fed to the water recovery column where the water and any residual hexane are removed as the overhead product under vacuum. A number of nitrogen bases and neutral oils, e.g. the pyridines, amines, nitriles and paraffins, form azeotropes with water. A substantial fraction of any of these components still present in the extract phase is therefore removed with the water as distillate. The phenolic compounds also form azeotropes with water. However, the azeotropic removal of the phenolic compounds as distillate is prevented to a large extent by the hydrogen bonds fomed between the phenolic compounds and the triethylene glycol in the extract. Therefore, a much smaller fraction of phenolic compounds than neutral oils and nitrogen bases is removed azeotropically with the water.

The distillate of the water recovery column therefore contains water as well as traces of hexane, neutral oils, nitrogen bases and phenolic compounds. A portion of the nitrogen bases, neutral oils and phenolic compounds are not water-soluble. The distillate therefore separates into an aqueous phase and an organic phase. Initially, it was planned to recycle the aqueous phase to the extraction column and combine the organic phase with the bottoms product of the hexane recovery column, which consists mainly of neutral oils and nitrogen bases. However, due to the preferential azeotropic removal of nitrogen bases and neutral oils, the ratio of these components to phenolic compounds in the aqueous phase is higher than the corresponding ratio in the original feed stream to the extraction column. It is therefore not desirable to recycle these components to the extraction column. Also, during the recovery of the water from the pilot plant extract, it was observed that the distillate of the water recovery column does not separate into two distinct phases, but forms an emulsion layer between the two phases. The separation of the aqueous and organic phases is therefore difficult. As a result, many of the water-insoluble neutral oils and nitrogen bases will be recycled to the extraction column along with the aqueous phase. A further consideration is that components such as methylpyridine are soluble in water and make up the bulk of the nitrogen bases removed during water recovery. It is preferable that these pyridines be removed from the process cycle.

Due to all the abovementioned factors, the water distillate is washed with a bleed stream from the distillate of the hexane recovery column. The hexane extracts a large portion of the neutral oils and nitrogen bases from the aqueous phase and facilitates phase separation. The aqueous phase can then be recycled to the extraction column and the hexane-rich phase to the hexane recovery column. The hexane is removed as distillate and the extracted organic compounds are removed from the process cycle as bottoms product along with the neutral oils, nitrogen bases and phenolic compounds in the raffinate.

The phenolic compounds, triethylene glycol and any neutral oils and nitrogen bases still present in the extract phase are recovered as the bottoms product of the water recovery column. It is imperative that all traces of water be removed from the bottoms product as the residual water cannot be removed in subsequent process steps and will therefore remain in the phenolic product as an impurity. However, as with the removal of hexane from the neutral oils and nitrogen bases, the removal of water from the triethylene glycol and phenolic compounds should pose no problem, as the minimum difference in boiling points is at least 80°C. It is obviously not necessary to separate the water from the hexane still present in the distillate, as both water and hexane are recycled to the extraction column as solvents.

The only potential problem in the water recovery process is the temperature in the reboiler. Care must be taken to ensure that this temperature does not exceed 210°C so

as to prevent decomposition of the triethylene glycol. The column is therefore operated under vacuum.

The bottoms product from the water recovery column, consisting of the phenolic compounds and triethylene glycol as well as trace amounts of nitrogen bases and neutral oils is fed to the solvent recovery column. The phenolic compounds, along with any residual neutral oils, nitrogen bases and water is removed as distillate. This distillate stream is the final phenolic product stream and is used as the basis for the calculation of phenolic product purity and recovery. The triethylene glycol is recovered as the bottoms product and is added to the overhead stream from the water recovery column and recycled to the extraction column.

The separation of the phenolic compounds from triethylene glycol should ordinarily be relatively straightforward as the difference in the boiling points of triethylene glycol and the higher boiling phenolic compounds such as the xylenols and ethylphenols is in excess of 55°C at atmospheric pressure. However, as with the water recovery column, the temperature in the reboiler of the solvent recovery should not exceed 210°C. The temperature in the reboiler can however be reduced by allowing a fraction of the phenolic compounds to remain in the bottoms stream. As the bottoms stream is recycled to the extraction column, these phenolic compounds will ultimately be recovered.

8.3 Simulations

The proposed process is simulated according to the flow sheet shown in Figure 8.3-1. The complete input file for the simulation of the proposed process and the relevant sections of the output file generated are given in Appendix D3.

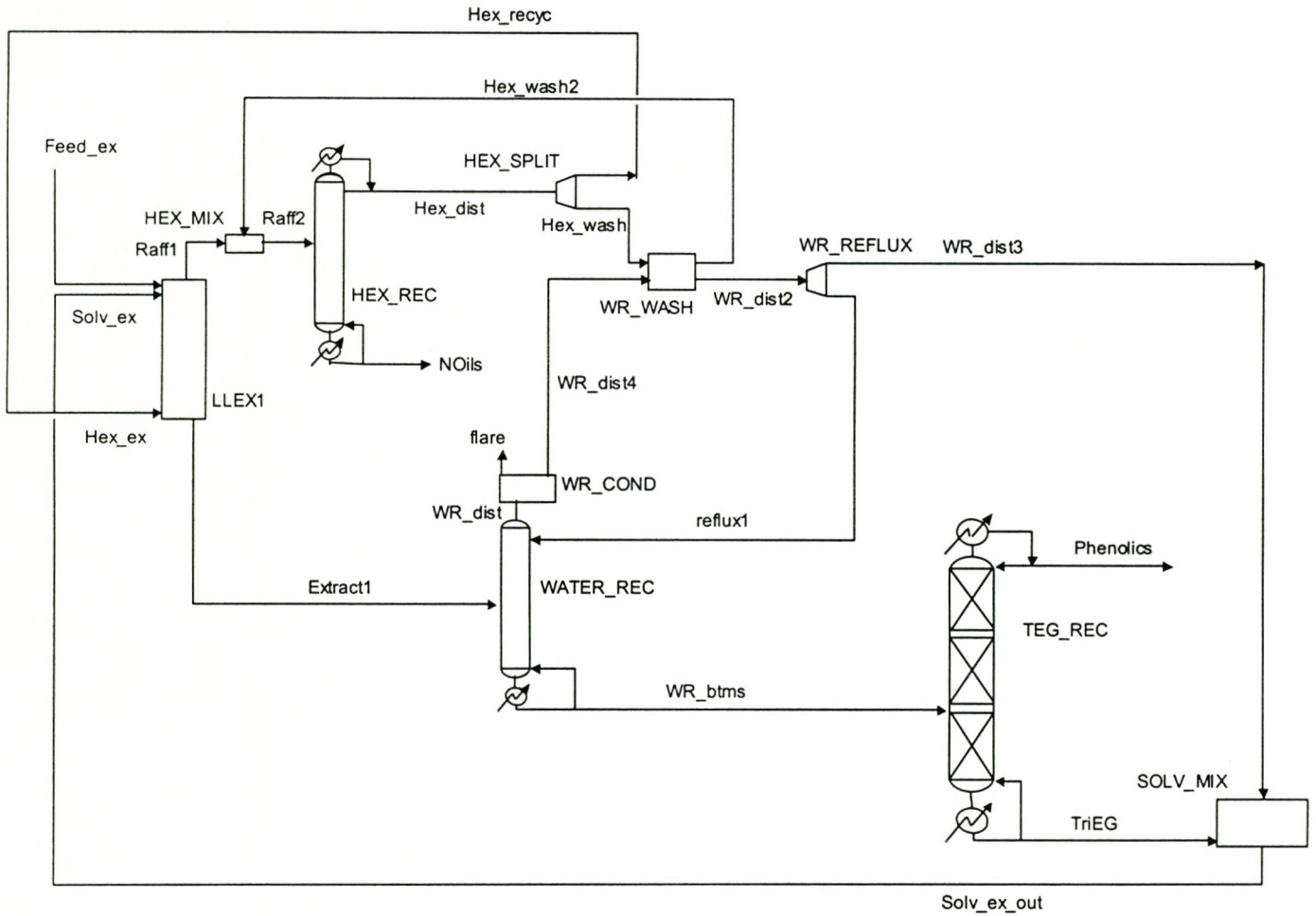


Figure 8.3-1. Simulated flow diagram of the proposed process

Table 8-1. Mass Flow Rates of Simulated Process Streams [kg/h]

STREAM ID	FEED_EX	HEX_EX	SOLV_EX	EXTRACT1	RAFF1	HEX_WASH2	RAFF2	HEX_DIST	NOILS	HEX_WASH
1 HEXANE	0.000	14998.512	0.000	23.947	14974.565	763.707	15738.240	15713.610	24.637	745.427
2 WATER	0.000	90.921	2277.060	2365.330	2.650	93.115	95.759	95.759	0.000	4.543
3 TEG	0.000	0.507	9141.242	9136.820	4.925	0.000	4.925	0.564	4.361	0.027
4 PHENOL	**677.949**	**0.000**	**70.622**	**715.031**	**33.539**	**5.580**	**39.099**	**0.001**	**39.097**	**0.000**
5 MCRESOL	**860.129**	**0.000**	**85.508**	**903.264**	**42.374**	**9.625**	**52.175**	**0.000**	**52.175**	**0.000**
6 PCRESOL	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**
7 24XYLNOL	**77.651**	**0.000**	**7.812**	**83.730**	**1.733**	**3.251**	**4.987**	**0.000**	**4.987**	**0.000**
8 35XYLNOL	**56.745**	**0.000**	**34.930**	**90.063**	**1.611**	**1.371**	**2.982**	**0.000**	**2.982**	**0.000**
9 34XYLNOL	**56.745**	**0.000**	**69.161**	**123.864**	**2.042**	**1.463**	**3.506**	**0.000**	**3.506**	**0.000**
10 ANILINE	2.987	0.000	0.810	3.252	0.545	0.293	0.837	0.000	0.837	0.000
11 OTOLUIDN	4.480	0.000	0.858	4.541	0.797	1.326	2.134	0.000	2.134	0.000
12 BNZNITRL	17.919	0.060	1.197	14.195	4.982	12.433	17.366	0.065	17.301	0.003
13 OTOLNTRL	44.798	0.000	0.150	1.031	43.918	0.506	44.424	0.000	44.423	0.000
14 ETMEPYR	38.825	0.000	0.150	12.797	26.178	10.754	36.919	0.000	36.919	0.000
15 135MBENZ	98.557	0.000	0.000	0.000	98.557	0.000	98.557	0.000	98.556	0.000
16 124MBENZ	92.583	0.000	0.000	0.000	92.583	0.000	92.584	0.000	92.583	0.000
17 INDANE	44.798	0.000	0.000	0.058	44.741	0.056	44.796	0.000	44.796	0.000
18 INDENE	89.597	0.000	0.000	0.003	89.597	0.003	89.600	0.000	89.599	0.000
19 NAPHTHLN	415.132	0.000	0.000	0.009	415.132	0.009	415.140	0.000	415.137	0.000
20 UNDECANE	107.516	0.000	0.000	0.000	107.516	0.000	107.516	0.000	107.515	0.000
21 DODECANE	313.589	0.000	0.000	6.232	307.357	6.225	313.581	0.000	313.579	0.000
TOTAL RATE, KG/HR	3000.000	15090.000	11689.500	13484.167	16295.340	909.715	17205.126	15810.000	1395.122	750.000
TEMPERATURE, °C	40.000	40.000	40.000	40.000	40.000	40.000	40.000	61.402	174.884	61.402
PRESSURE, KPA	101.325	101.325	101.325	146.825	101.325	20.000	101.325	101.325	112.325	101.325

Table 8-1. Mass Flow Rates of Simulated Process Streams [kg/h]

STREAM ID	HEX_RECYC	WR_BTMS	WR_DIST	WR_DIST2	WR_DIST3	WR_DIST4	FLARE	REFLUX1	PHENOLICS	TRIEG	SOL_EX_OUT
1 HEXANE	14968.182	0.000	23.962	0.029	0.015	18.303	5.658	0.015	0.000	0.000	0.015
2 WATER	91.216	0.900	4636.312	4547.038	2273.519	4635.617	0.695	2273.519	0.900	0.000	2273.519
3 TEG	0.537	9136.861	0.000	0.027	0.013	0.000	0.000	0.013	0.299	9136.586	9136.599
4 PHENOL	**0.001**	**644.129**	**135.845**	**130.248**	**65.124**	**135.828**	**0.018**	**65.124**	**639.495**	**4.628**	**69.752**
5 MCRESOL	**0.000**	**868.066**	**60.496**	**50.866**	**25.433**	**60.491**	**0.005**	**25.433**	**815.800**	**52.257**	**87.690**
6 PCRESOL	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**
7 24XYLNOL	**0.000**	**80.178**	**3.851**	**0.599**	**0.300**	**3.850**	**0.000**	**0.300**	**73.592**	**6.586**	**6.885**
8 35XYLNOL	**0.000**	**88.689**	**1.378**	**0.007**	**0.004**	**1.378**	**0.000**	**0.004**	**55.784**	**32.905**	**32.908**
9 34XYLNOL	**0.000**	**122.378**	**1.508**	**0.044**	**0.022**	**1.508**	**0.000**	**0.022**	**55.334**	**67.044**	**67.066**
10 ANILINE	0.000	2.150	1.907	1.613	0.807	1.906	0.000	0.807	2.150	0.000	0.807
11 OTOLUIDN	0.000	2.363	3.025	1.699	0.849	3.025	0.001	0.849	2.361	0.001	0.851
12 BNZNITRL	0.062	0.595	14.795	2.380	1.190	14.789	0.006	1.190	0.595	0.000	1.190
13 OTOLNTRL	0.000	0.069	1.416	0.911	0.456	1.416	0.000	0.456	0.069	0.000	0.456
14 ETMEPYR	0.000	1.901	11.048	0.300	0.150	11.047	0.001	0.150	1.901	0.000	0.150
15 135MBENZ	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
16 124MBENZ	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
17 INDANE	0.000	0.000	0.060	0.004	0.002	0.060	0.000	0.002	0.000	0.000	0.002
18 INDENE	0.000	0.000	0.003	0.000	0.000	0.003	0.000	0.000	0.000	0.000	0.000
19 NAPHTHLN	0.000	0.001	0.009	0.000	0.000	0.009	0.000	0.000	0.001	0.000	0.000
20 UNDECANE	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
21 DODECANE	0.000	0.001	6.231	0.000	0.000	6.225	0.006	0.000	0.001	0.000	0.000
TOTAL RATE, KG/HR	15060.000	10948.281	4901.844	4735.766	2367.883	4895.453	6.392	2367.883	1648.283	9300.006	11667.889
TEMPERATURE, C	61.402	206.235	59.856	40.000	40.000	40.000	40.000	40.000	79.632	194.348	40.000
PRESSURE, KPA	101.325	21.750	20.000	20.000	20.000	20.000	20.000	20.000	2.000	7.000	101.325

The flowsheet was simulated incrementally. Each major unit operation was solved and optimised before the following unit operation was added to the simulation. Once all four separation columns were optimised, the mass balances over the solvent and antisolvent streams entering and leaving the flowsheet were balanced. Parameters such as product stream flow rates were modified throughout the flowsheet to compensate for changes caused by the recycle streams.

The final mass flowrates of all the process streams in the simulated flowsheet are listed Table 8-1. The process streams are identified according to the stream names shown in Figure 8.3-1.

8.4 Extraction Column

8.4.1 Feed Stream

Ideally, the simulation of the proposed process should be based on a feed stream of the same composition as the typical industrial stream. However, as has been mentioned before, there are very few binary parameters available for multicomponent LLE systems and the estimations obtained from reduced VLE data are far from accurate.

Binary parameters for a number of the most prevalent components in the industrial feed stream have however been determined in the course of this study. The feed stream used for the simulation of the proposed process was therefore specified as a mixture of all the components for which binary parameters have been determined. It must however be borne in mind that the binary parameters for pairs of components that were not present in the same synthetic feed streams in the batch extractions were not determined. These unknown parameters will necessarily have to be estimated from the reduction of VLE data. The binary interaction parameters for all the feed components with respect to the solvents triethylene glycol, water and hexane are however known. Also, the general trends in the distribution of the various components between the two liquid phases should not differ significantly from those identified for the pilot plant tests and batch extractions. Discrepancies in the simulation results should therefore be easily identifiable.

Preliminary simulation results showed that the recovery of p-cresol in the extract phase was extremely low at approximately 45% for a range of different water to solvent ratios. The recoveries of the other phenolic components, including the xylenols, were in excess of 90% for the corresponding simulations. The recovery of p-cresol should be higher than that of the xylenols and m-cresol as its methyl group is further from the phenolic hydroxyl group than is the case in the other methyl-substituted phenols. I.e. the steric

hindrance offered by the methyl group to hydrogen bonding is less than in the other substituted phenols so the p-cresol molecule should be held more strongly in the solvent phase than the other cresol isomers and xylenol isomers. This is confirmed in the fact that the recovery of p-cresol was found to be slightly higher than that of m-cresol in the batch extraction tests. It was concluded that the prediction of the p-cresol recovery was inaccurate due to the relatively low number of known binary parameters applicable to p-cresol. It was therefore omitted from the simulation feed stream. The concentration of m-cresol was increased in order to account for the absence of p-cresol.

The composition of the feed stream used in the final simulations is therefore as shown in Table 8-2. Each component was originally selected to represent a group of components in an industrial feed stream when compiling the synthetic feed streams for the batch extractions. The specified concentrations of the various components reflect the concentration of the corresponding group of components in the industrial feed stream.

The flowrate of the feed stream was specified as 3000 kg/h. This value corresponds to an annual throughput of 20 000 tons.

Table 8-2. Percentage Composition of Synthetic Feed to Simulated Extraction Column

Component	[%]	Component	[%]
Phenol	22.7	5-et-2-me-pyridine	1.3
m-Cresol	28.8	Mesitylene	3.3
2,4-Xylenol	2.6	Pseudocumene	3.1
3,5-Xylenol	1.9	Indane	1.5
3,4-Xylenol	1.9	Indene	3.0
Aniline	0.1	Naphthalene	13.9
o-Toluidine	0.15	Undecane	3.6
Benzonitrile	0.6	Dodecane	10.5
o-Tolunitrile	1.5		

8.4.2 Thermodynamic Model

The thermodynamic model used was the three parameter NRTL equation as defined in Section 6.2. The binary parameters were specified as those obtained through the regression of batch extraction data. The matrix of known binary parameters is shown in Table 8-3 . It is clear from Table 8-3 that the number of unknown binary parameters applicable to p-cresol is significantly higher than the corresponding number of unknown binary parameters for the other components in the feed.

Table 8-3. Binary parameters b_{ij} for the system hexane(1) + water (2) + triethylene glycol (3) + phenol (4) + m-cresol (5) + p-cresol (6) +2,4-xylenol (7) + 3,5-xylenol (8) +3,4-xylenol (9) + aniline (10) + o-toluidine (11) + benzonitrile (12) + o-tolunitrile (13) + 5-et-2-me-pyridine (14) + mesitylene (15) + pseudocumene (16) + indane (17) + indene (18) + naphthalene (19) + undecane (20) + dodecane (21)

i	j																				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
1	0	1884	2164.5	1019.9	2163.7	3411.4	2276.2	3852.8	2798.5	481.5	51.95	2233	-83	2013	-1501	-438	662.8	253.3	231.4	-2142	4451
2	3579.9	0	-248	1403.2	819.63	1290.3	2544.8	3283.3	3178.4	950.4	884.6	2603	1071	2996	351	4457	2351	4044	3817	1843	6977
3	1559	6669	0	-267.6	-597.3	262.4	334.66	785.22	876.55	-450	-970	1336	-366	1440	-1419	472.1	356.8	-410	-360	-1581	-67.1
4	84.91	-211.3	-216.7	0						-709		996.5		1105	6656						
5	-568.3	270	4578.4		0	1320.7				1403	-789		-897			152.4		-598		4721	
6	-867.2	6800	3453.3		-857.2	0				-100			-1082								
7	4526.2	5853	3932.5				0	2602.1	2100								-857		7458		540.5
8	4099.8	2930	2850.1				2082.2	0	2574.9								933.4		991		-157
9	4831.7	3969	2176.4				1775.4	2488.5	0								599		1170		3295
10	503.2	62.63	278.6	1630	-616.9	145.27				0		1044	3208	1675	6692						
11	622.62	4489	1265.3		38.469						0		-372			-1003		-298		-440	
12	-131.2	6206	3561	1057.7						-130		0		2340	2330						
13	2566.9	538.5	2886.1		572.15	2284				4904	-1950		0			3765		-403		6190	
14	5960	5231	2546.4	1510.5						-955		2470		0	-199						
15	6366.4	750.5	1326.6	-261.3						-140		1759		1446	0						
16	1147.2	4746	5835.4		1871.9						15.29		-71.7			0		876.6		4392	
17	7109.7	4756	-68.27				846.48	4356.9	828.3								0		475		348.9
18	-375.3	636.4	487.42		3276						283.7		572.4			-1976		0		4503	
19	-326.2	699.9	536.95				9086.9	2556.5	1953								2685		0		4016
20	5842.7	3366	4254.8		340.62						-325		-780			-1843		-1057		0	
21	-1369	434	1382				9100.2	4963	5256								-602		119		0

The vapour and liquid viscosity of the feed, product and internal column streams were calculated with petrochemical component equations in ProII. LLE and VLE equilibrium K-values were calculated from NRTL LLE and VLE activity coefficients. Unavailable interaction parameters were estimated with UNIFAC group contribution methods.

8.4.3 Column Optimisation

It was specified that the solvent and feed stream enter at the top stage and hexane at the bottom stage of the column.

The extraction column was optimised at 40°C with regards to phenolic recovery and phenolic purity in the extract. The purity was calculated on a solvent-free basis. Optimisation of the column was by manipulation of the solvent to feed, hexane to feed and water to solvent ratios. The position at which the feed stream entered the column and the number of theoretical stages were also varied.

The optimum solvent ratios were determined as being a solvent to feed ratio of 3.05, a water to solvent ratio of 0.25 and a hexane to feed ratio of 5.0. These optimum solvent values correspond very well to those determined for the pilot plant tests.

The highest phenolic recovery and phenolic purity in the extract were obtained when the feed stream entered the column at the top with the feed. The optimum phenolic purity with respect to neutral oils and nitrogen bases was determined as being 97.85%. The corresponding phenolic recovery was 95.9%. These values are the optimum values in the context of the entire separation process, including the solvent recovery steps. A higher phenolic purity in the extract could be obtained at the cost of phenolic recovery by increasing the water to solvent ratio. This is however unnecessary as a significant proportion of the residual neutral oils are removed in subsequent process steps.

The optimum number of separation stages specified for the extraction column was seven. As was found in the pilot plant tests, an increase in the number of separation stages did not result in any noticeable decrease in the nitrogen bases and neutral oils remaining in the extract phase. As was the case with the pilot plant tests, aniline was the most difficult nitrogen base to remove from the extract. The lowest percentage of the mass of aniline entering the

extraction column that remained in the extract phase was 85%. This corresponds well to the percentage of feed aniline remaining in the extract of the pilot plant tests.

The flowrates of the feed, solvent, hexane, extract and raffinate process streams are listed in Table 8-1.

8.4.4 Column Dimensions

The diameter of the extraction column was initially estimated by assuming that the solvent phase droplets are spherical and fall through the continuous phase at a velocity calculated with Stokes Law [94]. The diameter of the droplets were assumed to be approximately 80 μm. The volumetric flowrates, densities and viscosities of both the solvent and antisolvent phases are supplied in the simulation output file for each theoretical stage. The settling velocity of the dispersed phase droplets and, consequently, the cross-sectional area of the column could therefore be determined for each theoretical stage. With this method, the maximum column diameter was determined as 1.23 m.

The simulated column diameter can also be estimated by scaling up the cross-sectional area of the pilot plant column, based on the relative flow rates in the two columns. The solvent to feed, water to solvent and hexane to feed ratios are almost identical for the simulated extraction process as they were in the pilot plant test carried out on the industrial feed stream. The ratio of the heavy phase to the light phase in the extraction columns can therefore be assumed to be similar. The relative velocity of the heavy phase to the light phase in the pilot plant test can be calculated as the total volumetric flowrate through the column divided by the cross-sectional area. It can then be assumed that the relative velocity of the heavy phase to the light phase in the simulation column is the same as that determined for the pilot plant column. The cross-sectional area of the simulated column can then be determined by dividing the total volumetric throughput of the column by the relative velocity of the two liquid phases. With this method, the diameter of the simulated column can be estimated as being approximately 1.93 m. This is significantly higher than the diameter calculated with Stokes Law. As the estimation of the larger diameter is based on actual measured process flowrates, it is accepted as being more accurate than the estimation based on Stokes Law.

The height of the extraction column was estimated based on the number of stages required to achieve the desired separation. The actual number of

stages required were calculated by dividing the number of theoretical stages required by the typical stage efficiency of the column. The typical stage efficiency was determined in Chapter 7 as being approximately 15 to 20 % for the synthetic pilot plant runs. I.e. approximately 35 to 45 actual stages are required. The height to diameter ratio of a standard separation stage in an industrial Kühni column is approximately 0.25 [19]. The column typically extends a further 2 m above and below the mixed section. The total column height is therefore between 14 and 18 m.

8.5 Hexane Recovery Column

A bleed stream from the distillate of the hexane recovery column was used to extract the organic components from the water distillate (see Figure 8.3-1). An isothermal flash unit operation carried out at 40°C was used to combine this stream with the raffinate stream exiting the extraction column. The combined streams were fed to the hexane recovery column, in which the hexane was distilled from the high-boiling components. The distillate from the hexane recovery column was split into two streams in the mass ratio of 95:5 by means of a splitter unit. This unit splits a single feed or mixture of feeds into two or more products of identical composition and phase. The bulk of the distillate stream was recycled to the extraction column, while the bleed stream was diverted to the flash drum of the water recovery column, before being recyled to the hexane recovery column.

The vapour-liquid equilibria in the column were modelled using the Wilson method. The VLE and LLE K-values were either calculated from NRTL VLE and LLE activity coefficients or, if these were unavailable, estimated using UNIFAC group contribution methods.

A kettle reboiler and bubble point condenser were specified for the column. The pressure in the condenser was specified as atmospheric pressure.

The hexane recovery column was optimised with regards to the hexane recovery and distillate purity. The column performance was specified according to the mass flow rate of the distillate stream. The optimum distillate composition was obtained by varying the number of trays, the position of the feed tray and the reflux ratio. The addition of an extra tray was considered justified if it led to a decrease in reboiler duty of more than 2%.

A hexane purity of 99.39% and recovery of 99.84% were obtained using 13 separation stages, including the condenser, and a reflux ratio of 0.5. The 0.61% impurity in the hexane was water. The feed entered on plate 8. The corresponding condenser and reboiler duties were 2400 and 2736 kW respectively.

According to the tray sizing calculations performed by ProII, the diameter of the column is 1.64 m and the trays are spaced 0.609 m apart. Assuming a tray efficiency of 65% and subtracting the condenser from the number of theoretical stages, the number of actual trays required is 18. An extra 2 m should be allowed for the sump and a further 1 m extension above the trayed section of the column. The total column height can thus be estimated as approximately 14 m.

8.5.1 Water Recovery Column

The extract from the extraction column was fed to the water recovery column, in which the distillation of the water from the extract phase was simulated. The pressure in the condenser was specified as 20 kPa.

The Wilson method was selected to model the vapour liquid equilibria in the water recovery column. The VLE and LLE K-values were calculated using the same method as for the hexane recovery column.

A bubble point condenser was initially specified for the water recovery column. The bubble-point temperature in the condenser was however predicted as 20°C at 20 kPa. This temperature cannot ordinarily be maintained with plant cooling water under South African conditions. The column was therefore simulated without a condenser. The only heater / cooler specified for the column was therefore the reboiler.

The condenser was modelled using two flash unit operations combined with a splitter unit (see Figure 8.3-1) The vapour stream exiting the top column of the water recovery column was condensed in an isothermal flash operation at 40°C and 20 kPa. A portion of this vapour stream was not condensed in the flash operation and was specified as a separate product stream. This stream consisted mostly of hexane and was drawn out of the system.

The simulation of the water recovery column confirmed the results obtained in the pilot plant tests in that a portion of the neutral oils, nitrogen bases and, to

a lesser extent, phenolic compounds were removed with the water as distillate by means of azeotropic distillation.

The percentage removal of the neutral oils, nitrogen bases and phenolic compounds from the bottoms product are listed in Table 8-4.

It can clearly be seen from Table 8-4 that the nitrogen bases and neutral oils are preferentially removed during water recovery while the phenolic compounds remain in the extract phase. This confirms the results obtained in the pilot plant tests, where the purity of the extract phase was significantly increased during water recovery with a very small reduction in the phenolic recovery.

Table 8-4 Percentage removal of phenolic compounds, nitrogen bases and aromatic nitriles from the extract phase during water recovery.

Component	Percentage Removal of Component [%]
Phenolic Compounds	10.1
Aniline	47.0
o-Toluidine	56.1
Benzonitrile	96.1
o-Tolunitrile	95.3
Et-me-pyridine	85.3
Mesitylene	100.0
Pseudocumene	100.0
Indane	99.9
Indene	99.9
Naphthalene	93.9
Undecane	100.0
Dodecane	100.0

While the removal of the nitrogen bases and neutral oils from the extract phase improves the purity of the phenolic product, these components would usually be recycled to the extraction column along with the recovered water. This is obviously undesirable as it increases the concentration of neutral oils and nitrogen bases in the extraction process. The water distillate is therefore washed with a hexane stream in order to remove the neutral oils and nitrogen bases before it is recycled to the extraction column.

The hexane extraction step was simulated as a flash unit algorithm. The water recovery distillate stream exiting the flash drum condenser of the water recovery column was therefore fed to a further flash unit operation where it was washed with a bleed stream from the hexane distillate.

The neutral oils and nitrogen bases that were present in significant amounts in the water distillate were aniline, o-toluidine, benzonitrile, o-tolunitrile and 5-et-2-me-pyridine. The percentage removal of these components from the distillate stream by the hexane stream is listed Table 8-5.

Table 8-5: Percentage removal of phenolic compounds, nitrogen bases and aromatic nitriles from the water recovery distillate by means of single step extraction with hexane.

Component	Percentage Removal of Component in Hexane Extraction [%]
Phenolic Compounds	10.5
Aniline	15.4
o-Toluidine	43.8
Benzonitrile	83.9
o-Tolunitrile	35.7
5-Et-2-me-pyridine	97.3

It can be seen from Table 8-5 that an appreciable amount of the neutral oils and nitrogen bases that were present in the distillate of the water recovery process are removed during the hexane extraction. In contrast, a relatively small percentage of the phenolic compounds are removed. I.e. the bulk of the phenolic compounds removed during the water recovery step are ultimately recycled to the extraction column, while a significant portion of the nitrogen bases and neutral oils removed are entirely removed from the recycled streams.

The aqueous phase exiting the hexane extraction step then entered a splitter unit where was split into two streams. One was recycled to the water recovery column as distillate and the other was recycled to the extraction column.

The trays used in the water recovery column were specified as being valve trays with a venturi-shaped orifice opening in the tray floor for pressure drop reduction.

The column was optimised with regards to the amount of water remaining in the bottoms product. Any water remaining in this process stream is regarded as an impurity in the final phenolic product.

The column was optimised by varying the number of trays, position of the feed tray and reflux ratio. Six trays, including the condenser were found to be optimum with the feed entering at tray four. The optimum reflux ratio was 0.25. Assuming a tray efficiency of 55% for the six theoretical trays, the actual number of trays required is 11. ProII calculated the diameter of the column as 1.98 m and the spacing between the trays as 0.609 m. The column height is thus 9.1 m, including 2 m for the sump and an extra 1 m above the trayed section of the column.

99.98% of the water in the extract phase was removed in the water recovery step. The residual water in the bottoms product comprises of less than 0.01% of the stream. The reboiler and condenser (flash) duties were determined as 4413 kW and 3189 kW respectively.

8.5.2 Solvent Recovery Column

The bottoms product from the water recovery column was fed to the solvent recovery column where the phenolic compounds and residual neutral oils and nitrogen bases were distilled off the triethylene glycol.

The thermodynamic system used for modelling the phase equilibria in the solvent recovery column was the same as that used for the water recovery column.

The column was operated under a vacuum of 2 kPa with a total pressure drop over the column equal to 1 kPa. These extreme vacuum conditions are necessary to prevent the reboiler temperature from exceeding 210°C while still effecting a separation between triethylene glycol and the phenolic compounds. Structured packing was used instead of plates in an attempt to further reduce the pressure drop over the column. The packing specified was Sulzer M250X structured packing for which an HETP value of 0.6 was assumed.

The condenser was specified as a bubble condenser. The value of the triethylene glycol recycle stream was specified so that a certain amount of phenolic compounds remained in the stream. The objective in mind is the subsequent reduction of the stream temperature. As the phenolic compounds remaining in the triethylene glycol bottoms stream are recycled to the extraction column, the final phenolic recovery is not decreased.

The triethylene glycol recovery column was optimised by manipulation of the flow rates specified for the product streams. The reboiler and condenser duties were determined as 1669 and 1453 kW respectively.

The optimum number of theoretical stages was determined as seven with the feed entering the column at stage four. The column diameter was calculated by ProII as being 1.88 m and the packed height as 3 m. Assuming two packed sections of 1.5 m each, a space of 1 m between the two sections for the entrance of the feed stream, a 2 m sump and a 2 m extension to accommodate the condenser, the total column height was estimated as 8 m.

The purity of the final phenolic compound product stream was 99.50% and the corresponding recovery relative to the feed of the extraction column was 94.84%. Both the purity and the recovery of the phenolic compounds fulfilled specifications.

In the pilot plant tests, the phenolic compounds recovered in the extract phase were not separated from the triethylene glycol. Final product purity and recovery was calculated only with respect to the neutral oils and nitrogen bases also present in the extract stream after water recovery. It can be seen from Table 8-1 that trace amounts of water and triethylene glycol remain in the phenolic product. If the water and solvent in the phenolic product are disregarded, the phenolic product purity increases to 99.57%. I.e. on a solvent-free basis, the simulated phenolic purity predicted is marginally lower than the 99.75% purity obtained in the pilot plant tests.

The phenolic recovery obtained in the simulated process corresponds well to the recovery obtained after one pilot plant extraction step.

It can therefore be concluded that, despite the relatively large number of unknown binary interaction parameters for the simulated feed stream, the results predicted correspond well to those obtained on pilot plant scale. The simulated process can therefore be used as a basis for further optimisation and process development.

8.5.3 Summary of Simulation Results

The dimensions, and number of theoretical stages required for the simulated separation columns are shown in Table 8-6.

Table 8-6. Column dimensions and number of stages required.

Column	Height [m]	Diameter [m]	Stages
Extraction Column	16	1.93	7
Hexane Recovery Column	14	1.64	12
Water Recovery Column	9	1.98	5
Solvent Recovery Column	8	1.88	7

The utility usage per kilogram of final phenolic product is shown in Table 8-7. The solvent losses and phenolic product purity and recovery are shown in Table 8-8. The solvent losses are expressed as the percentage difference between the mass of solvents in the streams entering the extraction column and in the streams exiting the flowsheet that would be recycled to the extracting column. The difference is expressed as a percentage of the solvent mass entering the extraction column.

Table 8-7. Utility usage for the hexane recovery column, Hex_rec, water recovery column Water_rec and solvent recovery column TEG_rec per kg of final phenolic product.

	Hex_rec	Water_rec	TEG_rec
Reboiler Duty [kJ / kg product]	5248	9640	3646
Saturated Reboiler Steam Pressure [bar]	17	34	34
Mass reboiler steam / mass product	2.7	5.3	2.0
Condenser Duty [kJ / kg product]	5976	6964	3174
Mass condenser water / mass product	119.6	138.9	72.6

Table 8-8 Percentage solvent losses and phenolic product purity and recovery

Evaluation Criteria	Mass Percentage
Phenolic Product Purity	99.50
Phenolic Recovery	94.84
Triethylene glycol loss over process	0.05
Hexane loss over process	0.20
Water loss over process	0.12

It can be concluded from Tables 8-6 and 8-8 that the proposed process is very successful from a technical point of view. The small columns required, low solvent losses and high phenolic recovery should make the process to be commercially attractive as well.

The results obtained with the simulations correspond well to those obtained in the pilot plant tests performed on an industrial feed stream. The simulation can therefore be used as a basis for evaluating the economic potential of the proposed process.

From the simulations and pilot plant tests based on a commercial feed stream it can be concluded that, using the proposed solvent system of triethylene glycol, water and hexane, a high phenolic recovery and high phenolic product purity can simultaneously be achieved for a wide-boiling feed stream with a range of different phenolic compounds, neutral oils and nitrogen bases. Solvent recovery is trivial and solvent losses are low. The solvents used are not toxic and the impact of the process on the environment should therefore be minimal.

In light of the above, it can be concluded that the proposed process fulfills the criteria stipulated at the outset.

CHAPTER 9. CONCLUSIONS

Triethylene glycol, hexane and water are proposed as a solvent system for the separation of phenolic compounds from neutral oils and nitrogen bases by means of liquid-liquid extraction.

9.1 Feed Components

An industrial heavy naphtha feed stream was analysed and the most prevalent components identified. Three synthetic feed streams were compiled to represent the industrial stream. The components in the respective feed streams were:

1. Phenol, aniline, benzonitrile, 5-et-2-me-pyridine and mesitylene
2. m-Cresol, o-toluidine, o-tolunitrile, pseudocumene, undecane and indene
3. 2,4-Xylenol, 3,5-xylenol, 3,4-xylenol, indane, dodecane and naphthalene

These components were selected to represent the different types of component in the industrial stream. The synthetic feed stream containing phenol was used as a basis for solvent selection.

9.2 Solvent Selection and Synthesis

Solvent selection was by means of computer-aided molecular design using a genetic algorithm. Solvents were evaluated on the basis of phenol recovery, phenol-benzonitrile separation factors, the presence of a liquid-liquid phase split and physical solvent properties such as boiling point and melting point.

High molecular weight molecules containing hydroxyl groups and ether groups were identified as effective solvents for the problem under investigation.

Batch extractions were performed on the phenol feed stream using a number of commercially available solvents containing the desired functional groups. It

was found that an increase in the number of hydroxyl groups contained in a molecule improved the efficiency of that molecule as a solvent, provided that the hydroxyl groups were positioned on the molecule backbone in such a way that they were available to form hydrogen bonds with the hydroxyl group of the phenolic molecules. The distance between solvent hydroxyl groups also had to be such that the solvent molecule could accommodate the large phenolic molecules.

Triethylene glycol was identified as the optimum commercially available solvent for a system containing water as a co-solvent and hexane as a countersolvent.

Two molecules analogous to the triethylene glycol molecule, but containing an extra hydroxyl group were synthesised from ethylene glycol and diethylene glycol. The ethylene glycol derivative contained two ether groups and three hydroxyl groups while the diethylene glycol derivative contained four ether groups and three hydroxyl groups. It was found that the former was a much less effective solvent than triethylene glycol while the latter was marginally more effective than triethylene glycol, especially with regards to the recovery of the 2,4-xylenol. However, as triethylene glycol is readily available, and as the improvement in separation efficiency using the synthesised solvent is slight, triethylene glycol was chosen as the solvent to be used in further investigations.

9.3 Optimum solvent ratios

A series of batch extractions was carried out on each of the three synthetic feed streams. The effect of the solvent to feed, water to solvent and hexane to feed ratio on the separation of the phenolic compounds from neutral oils and nitrogen bases as well as on phenolic recovery was investigated.

The effect of the various solvent ratios was found to be as follows:

Effect of solvent to feed ratio:

- An increase in the solvent to feed ratio leads to an increase in the recovery of phenolic compounds, nitrogen bases and neutral oils. This is especially significant at low water to solvent ratios and high hexane to feed ratios.

- The separation factors pertaining to phenolic compounds and nitrogen bases as well as those pertaining to phenolic compounds and neutral oils increase with an increase in the solvent to feed ratio, i.e. the increase in the phenolic compound recovery successfully counteracts the corresponding increase in nitrogen base and neutral oil recovery.
- An increase in the solvent to feed ratio beyond 3.0 does not result in any significant increase in phenolic recovery.

Effect of water to solvent ratio:

- An increase in the water to solvent ratio leads to a decrease in the recovery of phenolic compounds, nitrogen bases and neutral oils
- Xylenol isomers, in particular 2,4-xylenol, are more sensitive to an increase in the water to solvent ratio than either m-cresol or phenol
- The recovery of the xylenol isomers decreases sharply at water to solvent ratios in excess of 0.3
- The optimum water to solvent recoveries for the separation of phenolic compounds from nitrogen bases is 0.1 for batch extractions. The effect of the decrease in phenolic recovery with an increase in the water to solvent ratio has a disproportionately large effect on the separation factors. A higher water to solvent ratio is therefore justified for the removal of nitrogen bases from the extract phase
- Very low water to solvent ratios (<0.1) should not be used in conjunction with very low hexane to feed ratios (<0.5) and high water to solvent ratios (>2.0) as the percentage of feed neutral oils remaining in the extract phase becomes significant in this solvent region.

Effect of the hexane to feed ratio:

- An increase in the hexane to feed ratio leads to a decrease in the recovery of phenolic compounds, nitrogen bases and neutral oils.
- The effect of the hexane to feed ratio on phenolic recovery is most significant at high water to solvent ratios (>0.3).
- The decrease in phenolic recovery as the hexane to feed ratio is increased from 3.0 to 5.0 is not very large. The higher hexane to feed ratio is thus justified for the removal of nitrogen bases and neutral oils from the extract phase.

- The separation of phenolic compounds from nitrogen bases is more favourable as the hexane to feed ratio is increased.

It can therefore be concluded that the optimum solvent ratios are:

- Solvent to feed : 3.0
- Water to solvent : < 0.2
- Hexane to feed : 5.0

9.4 Thermodynamic modelling

Binary parameters for the NRTL model were determined through regression of the liquid-liquid equilibrium data generated by the batch extraction tests performed on the three synthetic feed streams as well as those generated for three additional multicomponent systems. The systems for which binary parameters were determined were as follows:

1. Phenol system:
   hexane + water + mesitylene + 5-et-2-me-pyridine + aniline + benzonitrile + phenol + triethylene glycol
2. m-Cresol system
   hexane + water + pseudocumene + undecane + indene + o-tolunitrile + o-toluidine + m-cresol + triethylene glycol
3. m-, p-Cresol system
   hexane + water + o-tolunitrile + m-cresol + p-cresol + triethylene glycol
4. Aniline-cresol system
   hexane + water + aniline + o-tolunitrile + m-cresol + p-cresol + triethylene glycol
5. Xylenol system
   hexane + water + indane + dodecane + naphthalene + 2,4-xylenol + 3,5-xylenol + 3,4-xylenol + triethylene glycol
6. Phenol-triethylene glycol monomethyl ether system
   hexane + water + mesitylene + 5-et-2-me-pyridine + aniline + benzonitrile + phenol + triethylene glycol monomethylether

Regression was by means of an algorithm incorporating a particle swarm method, the Levenberg-Marquardt algorithm and flash calculations.

The systems phenol, m-cresol, m-, p-cresol and aniline-cresol systems were modelled in the order given. The binary parameters determined for each system were used as the basis for modelling the following system. The binary parameters obtained for the phenol system were successfully used as a basis for the phenol - TEG monomethylether system.

9.5 Pilot plant tests

An adaption of the Kühni extraction column was built for a series of pilot plant tests. Both a synthetic feed stream consisting of aniline, o-tolunitrile, m-cresol and p-cresol and an industrial heavy naphtha stream were used in the pilot plant tests.

In the pilot plant tests performed on the synthetic feed stream it was found that the stage efficiency of the pilot plant column was very low at 15 to 20%. It was concluded that the low efficiency is due to the inherent behaviour of the solvent system and not to the hydrodynamic conditions within the extraction column. It was also discovered that there is a limnit to the amount of aniline that can be removed from the extract phase, even with the addition of extra separation stages.

The optimum performance of the pilot plant extraction column was achieved for:

1. a feed entry point at the top of the column with the solvent stream
2. high impeller speeds, approximately 320 rpm
3. a higher water to solvent ratio than was optimum for the batch extractions, i.e. approximately 0.25
4. high solvent to feed and hexane to feed ratios

The purity and recovery of the phenolic compounds achieved for the industrial feed stream after water recovery were very good at 99.76% and 91.1%. It was found that no significant increase in the purity of the phenolic compounds in the extract phase could be effected by a second multistage step. A significant fraction of the neutral oils and nitrogen bases remaining in the

extract phase were removed during the water recovery step without a significant corresponding decrease in phenolic recovery.

9.6 Conceptual process design

The entire separation process, including solvent recovery, was simulated and optimised with regards to phenolic product purity and recovery. As with the pilot plant tests, it was found that the specified purity of 99.5% could be achieved using extraction and distillation columns with few separation stages and low reflux ratios. The phenolic recovery achieved was in excess of 94%. The solvent losses predicted were negligible.

It can therefore be concluded that the proposed solvent process is highly effective for the separation of phenolic compounds from neutral oils. It has proved capable of processing a feed stream with a boiling range of 160 to 220°C in a single process. A phenolic product purity in excess of 99.5% can be achieved for reasonable solvent to feed ratios in few separation steps. A recovery in excess of 90% may be obtained simultaneously. Solvent recovery is straightforward and solvent losses are low.

9.7 Contribution to State of the Art

The present study yielded the following contributions to the state of the art in phenolic recovery from tar liquors :

1. **The proposal of the specific solvent system: triethylene glycol, water and hexane.**

Ethylene glycols have been investigated before as solvents for the recovery of phenolic compounds from tar liquors, but the emphasis has been on single solvent systems or dual solvent systems in which the feed is first contacted with the feed and the extract is subsequently contacted with a non-polar countersolvent. In this study, the simultaneous contacting of triethylene glycol, water and hexane was proposed. As a result, while previous studies concluded that triethylene glycol is not an effective solvent for the separation

of phenolic compounds from neutral oils and nitrogen bases, in this study the opposite was found to be true.

2. **A more thorough understanding of the interactions between the various feed components and the solvents**

Previous studies did not adopt a systematic approach in identifying the interaction between the feed components and the solvents investigated. In most cases, the investigations were based only on commercial feed streams and no attempt was made to isolate individual components and investigate their interaction with the various solvents in the system. In this study, the underlying reasons for the differences in the distribution of the various types of feed components between the two liquid phases were investigated more thoroughly.

3. **Thermodynamic modelling of a multicomponent system that is representative of an industrial feed stream**

Available LLE data for the components typically found in tar liquors are scarce and are on the whole limited to binary and ternary systems. Very few applicable binary interaction parameters have been published for the components and investigation and there is no guarantee that the published parameters are in fact the optimum parameters for the applicable component pairs. Most previous investigations have been based on commercial feed streams in which the individual component concentrations cannot be accurately determined. The fitting of thermodynamic models such systems studied is not possible. In this study, a thermodynamic model was fitted to multicomponent LLE systems that were representative of industrial systems. The model could successfully be used in the simulation of multistage extractions.

4. **The identification of role of the water recovery step in product purification and the extraction of organics from the water recovery distillate with a hexane bleed stream**

Despite the fact that many aqueous solvents have been proposed for the separation of phenolic compounds from neutral oils and nitrogen bases, no mention has been made of the fact that a significant fraction of the residual neutral oils and nitrogen bases in the extract can be removed during the water recovery step with no corresponding significant loss in phenolic recovery. This phenomenon has been identified and exploited in this study. The

removal of undesirable organic compounds from the distillate of the water recovery column with a bleed stream from the hexane recovery column distillate has also not been proposed before.

In conclusion, the proposed process is the first whereby a high phenolic recovery and product purity can be ahieved from a coal tar liquor without the need for post-purification of the phenolic product.

Further development of the process is recommended and has commenced in industry.

CHAPTER 10. RECOMMENDATIONS AND FUTURE WORK

The proposed process has been evaluated predominantly on technical grounds. A detailed cost estimate and profitability analysis will have to be done. A detailed design of the proposed process equipment is therefore required.

Designs of alternative processes should also be done for the same feedstock and conditions in order to assess the economic potential of the proposed process.

The influence of various feedstocks on the extraction process will have to be investigated. Pilot plant testing was carried out only on a heavy naphtha stream. The relative concentrations of the phenolic compounds, neutral oils and nitrogen bases in light naphtha, light creosote and heavy creosote streams differ from those in the heavy naphtha stream. The influence of the different feed compositions on optimum solvent ratios will have to be determined.

The phenolic product in this study was a mixture of all the phenolic compounds in the homologous series. This mixture will subsequently be fractionated into phenolic mixtures with narrower boiling ranges prior to the separation of the individual phenolic isomers. It is important to investigate the purity of the narrow-boiling phenolic fractions, as it is possible that the residual nitrogen bases and neutral oils in the wide-boiling fraction might concentrate in one of the narrow-boiling fractions. The extraction process would then have to be modified to compensate for this effect.

At present the aromatic compounds in naphtha and creosote streams are typically blended into petrol and diesel pools after hydrotreatment. The removal of the phenolic compounds from these streams will lead to a lower aromatic content of the petrol and diesel pools which might significantly affect the quality of the petrol and diesel produced. It might be preferable to recover fewer phenolic compounds in order to prevent adverse effects on processes using the feedstocks from which the phenolic compounds are to be recovered. The effect of phenolic recovery on existing plants must therefore be investigated.

The performance of the proposed solvent system in extractors such as mixer-settlers and mixer-settler columns should also be investigated.

Finally, a means for determining the missing binary parameters required to model a more comprehensive representative feed stream should ideally be found.

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APPENDIX A: Experimental Data

A1: Batch Extraction Data for Commercial Solvent Selection Tests

Table A1.1. Masses of Components added to Separating Funnels at 313.15K

Exp. ID	T [°C]	Masses of Components Added to Separating Funnels [g]								Masses of Resulting Phases [g]		ε_{MB} In/Out
		m_{hexane}	m_{water}	$m_{mesitylene}$	$m_{aniline}$	m_{phenol}	$m_{benzonitrile}$	m_{EMP}*	$m_{solvent}$	$m_{Solvent\ Phase}$	$m_{Hexane\ Phase}$	[%]
Solvent = Methanol												
Me1	40	60.010	15.246	1.363	1.042	10.701	1.003	1.015	15.292	42.638	61.751	-1.2
Solvent = 1-Methoxy-2-propanol												
mp1 c	40	45.091	1.687	1.390	1.032	10.662	1.034	1.013	15.126	25.825	49.719	-1.9
mp2 c	32	45.502	5.046	1.367	1.030	10.803	1.004	1.029	15.127	31.849	48.132	-1.1
mp3 a	32	45.100	10.012	1.363	1.004	10.835	1.047	1.018	15.059	36.631	47.366	-1.7
mp3 b	32	45.100	15.004	1.357	1.003	10.806	1.023	1.013	15.041	3 liquid phases formed		
mp3 e	32	75.100	15.060	1.357	1.066	10.860	1.017	1.048	15.026	3 liquid phases formed		
mp1 a	40	61.807	4.382	1.806	1.333	13.983	1.332	1.338	39.586	58.147	65.026	-1.9
mp1 b	40	45.100	10.071	1.386	1.066	10.813	1.024	1.010	31.679	55.271	47.373	0.5
mp2 b	32	58.950	26.553	1.779	1.308	13.783	1.298	1.025	39.116	79.654	63.646	-0.4
mp3 d	32	45.500	30.409	1.368	1.016	10.865	1.022	1.012	30.049	71.240	48.654	-1.1
mp1 d	40	45.354	5.027	1.381	1.017	10.795	1.019	1.001	45.170	67.084	39.827	-3.5
mp1 e	40	46.184	15.044	1.367	1.028	10.708	1.015	1.030	45.062	71.608	46.832	-2.5
Solvent = Triethylene glycol (TEG)												
6B	40	44.842	1.646	1.347	1.031	10.657	1.034	1.012	15.051	29.326	46.288	-1.3
1A	40	44.965	5.035	1.358	1.010	10.657	1.041	1.005	15.026	31.971	45.341	-3.5
2D	40	44.950	10.04	1.362	1.019	10.657	1.026	1.004	15.017	36.834	45.966	-2.7
6C	40	45.289	3.384	1.363	1.030	10.716	1.021	1.021	30.014	45.447	46.602	-1.9
9C	40	45.270	10.274	1.386	1.006	10.344	1.007	1.025	30.115	52.488	47.246	-0.7
4C	40	45.022	20.086	1.362	1.064	10.688	1.040	1.018	30.036	58.402	47.128	-2.3
7D	40	76.001	30.205	1.361	1.049	10.652	1.023	1.068	45.094	86.235	78.654	-0.9
6D	40	44.893	5.008	1.348	1.021	10.670	1.003	1.049	45.071	60.992	45.993	-2.8
9D	40	45.084	15.218	1.364	1.029	10.726	1.012	1.034	45.070	72.845	45.818	-1.6

*5-Ethyl-2-methyl-pyridine

Table A1.1. Masses of Components added to Separating Funnels at 313.15K(Cont.)

Exp. ID	T [°C]	Masses of Components In [g]								Masses of Resulting Phases [g]		ε_{MB} In/Out
		m_{hexane}	m_{water}	$m_{mesitylene}$	$m_{aniline}$	m_{phenol}	$m_{benzonitrile}$	m_{EMP}*	$m_{solvent}$	$m_{Solvent\ Phase}$	$m_{Hexane\ Phase}$	[%]
Solvent = Triethylene glycol monomethylether												
e1a	40	46.300	10.004	1.760	1.007	11.061	1.036	1.049	30.587	54.142	47.130	-1.5
e1b	40	46.100	20.465	1.403	1.010	10.673	1.006	1.006	30.348	63.114	47.848	-0.9
e1c	40	46.200	5.009	1.426	1.033	10.990	1.009	1.045	15.425	32.863	47.352	-2.3
e2a	40	46.700	15.031	1.392	1.016	10.883	1.021	1.015	46.099	75.409	46.886	-0.7
e2c	40	45.800	5.037	1.413	1.004	10.872	1.004	1.013	45.856	65.082	44.776	-1.9
e3a	40	22.600	1.695	0.668	0.502	5.557	0.518	0.505	7.759	16.379	22.613	-2.0
e3c	40	22.500	5.313	0.695	0.515	5.407	0.528	0.514	7.606	18.834	23.458	-1.8
e5b	40	75.500	5.014	1.452	1.008	10.692	1.049	1.007	15.101	32.434	77.630	-0.7
e5d	40	76.300	10.482	1.363	1.003	10.943	1.039	1.016	15.100	37.777	77.907	-1.3
Solvent = Tetraethylene glycol dimethylether (Tetraglyme)												
tg1a	40	31.600	3.508	0.947	0.712	7.544	0.737	0.712	10.533	23.296	30.989	-3.6
tg1b	40	32.500	7.143	0.973	0.708	7.730	0.717	0.697	21.336	36.280	34.278	-1.7
tg1c	40	31.200	10.141	0.969	0.706	7.513	0.716	0.722	31.609	49.946	33.243	-0.5
tg1d	40	42.300	5.532	0.746	0.562	5.890	0.742	0.557	21.088	31.885	43.829	-2.2
tg1e	40	42.200	11.270	0.869	0.572	5.961	0.552	0.590	21.307	38.135	42.856	-2.8
Solvent = Acetone												
A 1a	30	64.100	15.010	1.355	1.034	10.978	1.005	1.006	45.902	3 liquid phases formed		
A 1b	30	45.100	10.026	1.366	1.027	10.702	1.023	1.025	30.430	10.633	66.668	-2.1
A 1c	30	78.800	45.573	1.358	1.039	10.742	1.008	1.019	15.171	3 liquid phases formed		
A 1d	30	77.500	30.210	1.387	1.011	10.825	1.004	1.016	60.214	97.348	83.207	-1.4
A 2a	30	45.500	1.665	1.362	1.001	10.654	1.016	1.014	15.319	19.983	55.623	-2.5
A 2b	30	61.000	1.708	1.357	1.034	10.660	1.013	1.010	15.081	16.979	74.709	-1.3
A 2c	30	45.100	3.327	1.395	1.035	10.622	1.046	1.041	30.037	30.118	62.314	-1.3
Solvent = Acetylacetone												
Aa1a	30	45.102	1.675	1.376	1.048	10.765	1.040	1.019	15.206	3 liquid phases formed		
Aa1b	30	45.200	3.365	1.378	1.016	10.856	1.011	1.030	30.735	2.675	89.416	-2.6
Aa1c	30	45.023	15.06	1.394	1.014	10.824	1.010	1.014	45.815	15.198	104.813	-0.9
Aa1d	30	30.321	3.350	1.361	1.028	10.765	1.023	1.087	30.679	3 liquid phases formed		
Aa1e	30	45.901	10.291	1.395	1.260	10.986	1.033	1.003	30.707	3 liquid phases formed		

*5-Ethyle-2-methyl pyridine

Table A1.2 : Equilibrium Composition of Solvent and Hexane Phases for Commercial Solvent Selection Batch Extractions at 313.15K

	Masses of components in Solvent Phase										Masses of components in Hexane Phase									
Exp. ID	m_{hexane}	m_{water}	$m_{mesi-tylene}$	$m_{aniline}$	m_{phenol}	$m_{benzo-nitrile}$	$m_{etme\ Pyridine}$	$m_{solvent}$	$m_{solvent\ Phase}$	ε_{SP} [%]	m_{hexane}	m_{water}	$m_{mesi-tylene}$	$m_{aniline}$	m_{phenol}	$m_{benzo-nitrile}$	$m_{etme\ Pyridine}$	$m_{solvent}$	$m_{hexane\ Phase}$	ε_{HP} [%]
Solvent = Methanol																				
me1e	3.887	15.246	0.042	0.836	9.380	0.621	0.470	12.222	42.705	0.2	57.200	0.000	1.452	0.178	1.132	0.400	0.551	3.955	64.869	1.1
Solvent = 1-Methoxy-2-propanol																				
mp1 c	4.913	1.687	0.255	0.677	7.384	0.599	0.523	9.951	25.988	0.6	40.822	0.001	1.149	0.328	3.023	0.430	0.464	4.743	50.960	2.5
mp2 c	2.098	5.046	0.160	0.841	9.438	0.702	0.633	12.886	31.804	-0.1	43.549	0.001	1.198	0.171	1.264	0.291	0.399	2.001	48.874	1.5
mp3 a	1.267	10.012	0.106	0.863	9.700	0.696	0.581	13.997	37.223	1.6	43.482	0.001	1.260	0.147	1.050	0.317	0.436	1.176	47.868	1.1
mp3 b	3 Liquid Phases formed																			
mp3 e	3 Liquid Phases formed																			
mp1 a	12.027	4.382	0.565	1.003	10.709	0.895	0.807	29.020	59.409	2.2	49.907	0.002	1.207	0.322	3.166	0.409	0.540	9.408	64.960	-0.1
mp1 b	3.179	10.077	0.216	0.934	10.062	0.781	0.684	28.010	53.943	-2.4	40.356	0.001	1.179	0.148	1.036	0.257	0.348	3.133	46.457	-1.9
mp2 b	1.461	26.553	0.130	1.126	12.599	0.918	0.604	35.603	78.993	-0.8	59.096	0.000	1.653	0.181	1.115	0.391	0.436	2.640	65.511	2.9
mp3 d	1.003	30.005	0.095	0.866	9.600	0.648	0.521	26.250	68.988	-3.2	42.100	0.001	1.279	0.132	1.201	0.350	0.523	2.600	48.186	-1.0
mp1 d	14.236	5.027	0.598	0.823	9.112	0.788	0.728	36.197	67.510	0.6	29.531	0.002	0.795	0.181	1.709	0.235	0.272	8.141	40.863	2.6
mp1 e	3.275	15.044	0.234	0.910	9.792	0.797	0.722	41.030	71.804	0.3	41.879	0.034	1.128	0.111	0.809	0.218	0.317	3.598	48.397	3.3
Solvent = Triethylene glycol																				
4C	0.133	19.962	0.028	0.884	9.700	0.622	0.363	29.034	60.726	4.0	41.903	0.016	1.325	0.143	0.676	0.442	0.685	0.048	45.238	-4.0
6C	0.496	3.304	0.131	0.917	10.644	0.698	0.569	29.626	46.385	2.1	43.421	0.006	1.207	0.118	0.452	0.324	0.47	0.026	46.024	-1.2
9C	0.340	10.293	0.044	0.913	10.066	0.67	0.508	30.048	52.882	0.8	43.537	0.008	1.357	0.121	0.462	0.349	0.531	0.01	46.375	-1.8
1A	0.360	4.938	0.058	0.862	9.911	0.662	0.484	15.068	32.343	1.2	41.314	0.019	1.275	0.145	0.639	0.392	0.546	0.148	44.478	-1.9
2D	0.241	9.914	0.044	0.820	9.740	0.575	0.397	14.886	36.617	-0.6	43.559	0.029	1.369	0.171	0.816	0.446	0.622	0.086	47.098	2.5
6B	0.590	1.686	0.106	0.897	10.089	0.707	0.549	14.862	29.486	0.5	44.658	0.008	1.237	0.133	0.581	0.332	0.459	0.026	47.434	2.5
7D	0.331	30.654	0.032	0.881	9.907	0.504	0.328	45.593	88.230	2.3	76.861	0.010	1.291	0.178	0.640	0.528	0.716	0.023	80.247	2.0
6D	0.612	5.008	0.160	0.943	10.530	0.745	0.646	44.740	63.384	3.9	43.797	0.008	1.197	0.07	0.238	0.239	0.384	0.002	45.935	-0.1
9D	0.61	15.020	0.062	0.954	10.271	0.727	0.552	44.652	72.848	0.0	43.912	0.005	1.332	0.088	0.308	0.317	0.49	0.138	46.590	1.7

Table A1.2 : Equilibrium Composition of Solvent and Hexane Phases for Commercial Solvent Selection Batch Extractions at 313.15K

	Masses of Components in Solvent Phase										Masses of Components in Hexane Phase									
Exp. ID	m_{hexane}	m_{water}	$m_{mesi-tylene}$	$m_{aniline}$	m_{phenol}	$m_{benzo-nitrile}$	$m_{etme Pyridine}$	$m_{solvent}$	$m_{solvent Phase}$	ε_{SP} [%]	m_{hexane}	m_{water}	$m_{mesi-tylene}$	$m_{aniline}$	m_{phenol}	$m_{benzo-nitrile}$	$m_{etme Pyridine}$	$m_{solvent}$	$m_{hexane Phase}$	ε_{HP} [%]
Solvent = Triethylene glycol monomethylether																				
e1a	0.867	9.951	0.136	0.919	10.781	0.770	0.654	29.809	53.887	-0.5	44.385	0.014	1.580	0.073	0.287	0.248	0.396	0.182	47.165	0.1
e1b	0.437	20.291	0.058	0.898	10.298	0.675	0.533	30.524	63.715	1.0	45.620	0.012	1.351	0.095	0.376	0.306	0.464	0.144	48.368	1.1
e1c	1.019	4.883	0.100	0.892	10.472	0.717	0.634	15.010	33.727	2.6	44.278	0.012	1.331	0.111	0.471	0.291	0.441	0.083	47.019	-0.7
e2a	1.448	15.459	0.116	0.922	10.750	0.793	0.626	46.011	76.124	0.9	44.039	0.013	1.295	0.063	0.302	0.193	0.380	0.059	46.344	-1.2
e2c	4.718	5.076	0.284	0.970	10.460	0.842	0.744	44.197	67.291	3.4	42.597	0.011	1.116	0.037	0.169	0.130	0.277	0.545	44.881	0.2
e3a	0.918	1.695	0.068	0.441	5.208	0.364	0.310	7.649	16.653	1.7	21.016	0.004	0.590	0.052	0.222	0.141	0.203	0.112	22.339	-1.2
e3c	0.339	5.198	0.033	0.448	4.963	0.344	0.261	7.435	19.020	1.0	22.592	0.006	0.669	0.063	0.312	0.174	0.262	0.020	24.096	2.7
e5b	1.281	4.930	0.073	0.846	9.932	0.632	0.482	15.054	33.230	2.5	74.605	0.018	1.340	0.156	0.638	0.406	0.554	0.163	77.879	0.3
e5d	0.583	10.351	0.028	0.829	9.849	0.517	0.431	15.324	37.911	0.4	76.575	0.019	1.336	0.187	0.931	0.486	0.597	0.152	80.284	3.1
Solvent = Tetraethylene glycol dimethylether (Tetraglyme)																				
tg1a	1.322	3.425	0.106	0.644	7.222	0.559	0.436	10.003	23.718	1.8	29.868	0.022	0.862	0.083	0.399	0.189	0.280	0.461	32.164	3.8
tg1b	1.427	7.002	0.123	0.656	7.320	0.559	0.435	19.612	37.135	2.4	31.677	0.029	0.842	0.065	0.361	0.155	0.257	1.249	34.634	1.0
tg1c	1.623	10.189	0.137	0.654	7.292	0.581	0.477	29.963	50.915	1.9	30.349	0.034	0.831	0.048	0.300	0.139	0.243	1.765	33.709	1.4
tg1d	1.378	5.484	0.063	0.493	5.454	0.522	0.295	19.145	32.833	3.0	40.454	0.041	0.676	0.073	0.423	0.217	0.267	2.143	44.294	1.1
tg1e	0.826	11.212	0.051	0.500	5.613	0.375	0.291	19.821	38.689	1.5	40.902	0.033	0.822	0.074	0.381	0.184	0.299	1.371	44.065	2.8
Solvent = Acetone → Reacts with Aniline in Feed																				
Solvent = Acetylacetone → Reacts with Aniline in Feed																				

A2 Batch Extraction Data for Synthesised Solvent Selection Tests

Table A2.1: Masses of Components added to Separating Funnels at 313.15K

Exp. ID	Solvent	Masses of components into separating funnels [g]							Resulting Phases [g]		
		m_{Hexane}	m_{Water}	$m_{o\text{-}Tolunitrile}$	$m_{o\text{-}Toluidine}$	$m_{m\text{-}Cresol}$	$m_{2,4\text{-}Xylenol}$	$m_{Solvent}$	$m_{Solvent\ Phase}$	$m_{Hexane\ Phase}$	$\varepsilon_{MB\ In/Out}$
Solvent : Feed = 1.0; Hexane : Feed = 4.0; Water : Solvent = 0.11 (Mass Ratios)											
s1a	EgD	26.261	0.894	1.103	0.000	5.475	0.000	6.560	13.023	26.592	-1.7
s1b	TEG	58.800	1.989	2.453	0.000	12.192	0.000	15.136	30.773	58.745	-1.2
s1g	DiEGD	26.600	0.906	1.120	0.000	5.474	0.000	6.560	13.084	26.569	-2.5
s1c	Tetra EG	26.293	0.899	1.104	0.000	5.483	0.000	6.571	12.682	28.053	1.0
s1e	Tetrglyme	52.522	1.800	2.215	0.000	10.990	0.000	13.232	26.599	51.855	-2.9
s1d	Glycerol	26.253	0.906	1.101	0.000	5.497	0.000	6.541	13.504	26.187	-1.5
s1f	Methanol	52.632	1.810	2.273	0.000	11.011	0.000	14.000	29.312	49.820	-3.2
Solvent : Feed = 3.0; Hexane : Feed = 4.0; Water : Solvent = 0.33 (Mass Ratios)											
s2b	TEG	48.756	12.399	2.058	2.031	0.000	8.316	36.070	58.580	48.904	-2.0
s2a	DiEGD	24.320	6.051	1.013	1.014	0.000	3.998	18.032	28.614	24.058	-3.2
s2c	Tetra EG	48.625	12.230	2.034	2.023	0.000	8.032	36.383	58.766	49.516	-1.0
s2d	Glycerol	48.208	12.166	2.043	2.086	0.000	8.291	36.195	48.476	58.567	-1.8
Solvent : Feed = 1.0; Hexane : Feed = 5.0; Water : Solvent = 0.11 (Mass Ratios)											
s3b	TEG	24.001	1.718	1.000	1.017	0.000	4.017	12.387	19.332	24.340	-1.1
s3a	DiEGD	22.754	1.642	0.956	0.959	0.000	3.803	11.635	17.825	23.103	-2.0
s3c	Tetra EG	24.007	1.367	1.018	1.016	0.000	4.008	12.165	18.724	23.720	-2.6
s3e	Tetrglyme	24.002	1.338	1.011	1.070	0.000	4.043	12.386	18.105	24.044	-3.9
s3d	Glycerol	24.107	1.347	1.007	1.017	0.000	4.030	12.462	13.089	30.851	-0.1
s3f	Methanol	24.030	1.362	1.012	1.051	0.000	4.011	12.109	20.702	21.367	-3.5
Solvent : Feed = 0.6; Hexane : Feed = 5.1; Water : Solvent = 1.4 (Molar Ratios)											
s1a	EGD	26.261	0.894	1.103	0.000	5.475	0.000	6.560	13.023	26.592	-1.7
s4a	TEG	34.478	1.166	1.443	0.000	7.179	0.000	7.166	16.309	33.787	-2.6
s4e	DiEGD	23.770	0.839	1.009	0.000	4.912	0.460	8.896	15.264	23.639	-2.5
s4b	Tetra EG	26.662	0.928	1.103	0.000	5.503	0.000	7.110	14.141	26.159	-2.4
s4d	Tetrglyme	26.261	0.892	1.105	0.000	5.493	0.000	8.176	14.731	26.013	-2.8
s4c	Glycerol	26.701	0.905	1.125	0.000	5.438	0.000	3.400	7.988	28.516	-2.8
s4f	Methanol	53.772	1.879	2.229	0.000	10.950	0.000	2.608	13.834	54.674	-4.1
Solvent : Feed = 1.3; Hexane : Feed = 5.6; Water : Solvent = 5.0 (Molar Ratios)											
s5a	TEG	24.750	6.109	1.023	1.027	0.000	4.006	10.131	20.446	25.609	-2.1
s2a	DiEGD	24.320	6.051	1.013	1.014	0.000	3.998	18.032	28.614	24.058	-3.2
s5b	Tetra EG	24.342	6.138	1.016	1.013	0.000	3.995	13.471	24.265	24.863	-1.7
s5d	Tetrglyme	24.602	6.129	1.013	1.007	0.000	4.020	15.044	3 phases formed		
s5c	Glycerol	24.754	6.079	1.011	1.038	0.000	4.002	6.412	11.866	28.864	-5.9
									3 phases formed		
s5e	MeOH	98.254	24.452	4.033	4.037	0.000	15.920	8.585	31.122	119.990	-2.7
Solvent : Feed = 0.9; Hexane : Feed = 5.4; Water : Solvent = 2.1 (Molar Ratios)											
s6d	TEG	22.666	1.644	0.959	0.954	0.000	3.883	6.549	12.896	22.881	-2.4
s3a	DiEGD	22.754	1.642	0.956	0.959	0.000	3.803	11.635	17.825	23.103	-2.0
s6c	Tetra EG	22.948	1.647	0.956	0.960	0.000	3.811	9.436	14.909	23.895	-2.4
s6b	Tetrglyme	22.574	1.660	0.977	0.974	0.000	3.981	9.672	3 phases formed		
s6a	Glycerol	22.826	1.722	0.956	0.958	0.000	3.819	4.062	5.814	28.057	-1.4
s6e	Methanol	81.908	5.940	3.545	3.456	0.000	13.711	5.012	7.864	104.174	-1.4
Solvent : Feed = 0.8; Hexane : Feed = 3.0; Water : Solvent = 7.5 (Molar Ratios)											
s7b	TEG	15.878	6.667	1.018	1.031	0.000	4.731	7.465	3 phases formed		
s7a	DiEGD	15.928	6.611	1.006	1.014	0.607	4.698	13.065	25.364	16.538	-2.4
s7d	Tetra EG	15.888	6.736	1.007	1.038	0.000	4.689	9.626	21.831	15.215	-5.0
s7e	Tetrglyme	39.956	16.542	2.534	2.540	0.000	11.906	27.661	3 phases formed		
s7f	Methanol	81.682	33.945	5.172	5.197	0.000	24.418	8.107	38.362	118.455	-1.1

Table A2.2 : Equilibrium Composition of Solvent and Hexane Phases for Synthesised Solvent Selection Batch Extractions at 313.15K

Exp. ID	Solvent	Masses of Components in Solvent Phase [g]								Masses of Components in Hexane Phase [g]							
		m_{Hexane}	m_{Water}	$m_{o\text{-}Tolunitrile}$	$m_{o\text{-}Toluidine}$	$m_{m\text{-}Cresol}$	$m_{2,4\text{-}Xylenol}$	$m_{Solvent}$	ESP	m_{Hexane}	m_{Water}	$m_{o\text{-}Tolunitrile}$	$m_{o\text{-}Toluidine}$	$m_{m\text{-}Cresol}$	$m_{2,4\text{-}}$	$m_{Solvent}$	EHP
Solvent : Feed = 1.0; Hexane : Feed = 4.0; Water : Solvent = 0.11 (Mass Ratios)																	
s1a	EgD	0.820	0.951	0.519	0.000	4.702	0.000	6.560	4.1	25.321	0.007	0.617	0.000	0.632	0.000	0.005	0.0
s1b	TEG	1.613	2.062	1.344	0.000	11.428	0.000	15.136	2.6	55.617	0.007	1.176	0.000	0.562	0.000	0.000	-2.4
s1g	DiEGD	0.748	0.909	0.540	0.000	5.108	0.000	6.459	5.2	25.400	0.005	0.587	0.000	0.363	0.000	0.001	-0.8
s1c	Tetra EG	0.100	0.869	0.524	0.000	5.036	0.000	6.212	0.5	26.000	0.005	0.548	0.000	0.309	0.000	0.214	-3.5
s1e	Tetraglyme	5.078	1.716	1.340	0.000	9.400	0.000	10.003	3.5	45.865	0.080	0.914	0.000	1.515	0.000	2.671	-1.6
s1d	Glycerol	0.274	0.918	0.350	0.000	4.388	0.000	7.082	-3.6	25.240	0.018	0.750	0.000	1.102	0.000	0.000	3.5
s1f	Methanol	6.897	1.685	1.451	0.000	8.793	0.000	11.589	3.8	44.000	0.097	0.886	0.000	2.321	0.000	2.045	-0.9
Solvent : Feed = 3.0; Hexane : Feed = 4.0; Water : Solvent = 0.33 (Mass Ratios)																	
s2b	TEG	1.222	12.712	0.985	1.534	0.000	7.701	35.529	1.9	48.064	0.010	1.091	0.447	0.000	0.605	0.036	2.8
s2a	DiEGD	0.334	6.209	0.415	0.747	0.000	3.609	18.032	2.6	22.929	0.008	0.591	0.282	0.000	0.399	0.000	0.6
s2c	Tetra EG	0.862	12.488	1.003	1.606	0.000	7.608	36.000	1.4	48.064	0.010	1.031	0.403	0.000	0.482	0.008	1.0
s2d	Glycerol	0.448	12.361	0.020	0.148	0.000	0.658	35.789	2.0	46.139	0.116	2.011	1.910	0.000	7.534	0.000	-1.5
Solvent : Feed = 1.0; Hexane : Feed = 5.0; Water : Solvent = 0.11 (Mass Ratios)																	
s3b	TEG	0.654	1.808	0.528	0.814	0.000	3.723	12.387	3.0	22.489	0.006	0.453	0.196	0.000	0.254	0.004	-3.9
s3a	DiEGD	0.145	1.711	0.453	0.703	0.000	3.460	11.653	1.7	22.196	0.005	0.505	0.237	0.000	0.313	0.023	0.8
s3c	Tetra EG	0.167	1.479	0.522	0.810	0.000	3.986	11.653	-0.6	22.700	0.003	0.465	0.217	0.000	0.111	0.305	-0.1
s3e	Tetraglyme	1.119	1.285	0.646	0.814	0.000	3.404	11.842	5.6	22.547	0.037	0.342	0.247	0.000	0.733	0.000	-0.6
s3d	Glycerol	0.148	1.283	0.010	0.037	0.000	0.188	11.987	4.3	23.205	0.026	1.023	0.979	0.000	3.989	0.000	-5.3
s3f	Methanol	2.833	1.366	0.761	0.907	0.000	3.346	11.267	-1.1	19.906	0.033	0.264	0.134	0.000	0.641	0.721	1.6
Solvent : Feed = 0.6; Hexane : Feed = 5.1; Water : Solvent = 1.4 (Molar Ratios)																	
s1a	EGD	0.820	0.951	0.519	0.000	4.702	0.000	6.560	4.1	24.893	0.007	0.617	0.000	0.632	0.000	0.005	-1.6
s4a	TEG	0.454	1.191	0.783	0.000	6.600	0.000	7.166	-0.7	33.170	0.006	0.660	0.000	0.426	0.000	0.000	1.4
s4e	DiEGD	0.200	0.847	0.494	0.000	4.652	0.000	8.896	-1.1	23.222	0.003	0.489	0.000	0.241	0.000	0.000	1.3
s4b	Tetra EG	0.427	0.956	0.605	0.000	5.184	0.000	7.110	1.0	25.106	0.004	0.488	0.000	0.253	0.000	0.409	0.4
s4d	Tetraglyme	1.893	0.837	0.670	0.000	4.543	0.000	6.500	-2.0	23.518	0.050	0.446	0.000	0.920	0.000	1.601	2.0
s4c	Glycerol	0.289	0.912	0.322	0.000	3.247	0.000	3.400	2.3	26.412	0.032	0.807	0.000	2.153	0.000	0.010	3.2
s4f	Methanol	0.704	1.877	1.062	0.000	7.365	0.000	2.344	-3.5	51.637	0.073	1.165	0.000	3.620	0.000	0.427	4.1

Table A2.2 : Equilibrium Composition of Solvent and Hexane Phases for Synthesised Solvent Selection Batch Extractions at 313.15K

Exp. ID	Solvent	Masses of Components in Solvent Phase [g]								Masses of Components in Hexane Phase [g]							
		m_{Hexane}	m_{Water}	$m_{o\text{-}Tolunitrile}$	$m_{o\text{-}Toluidine}$	$m_{m\text{-}Cresol}$	$m_{2,4\text{-}Xylenol}$	$m_{Solvent}$	ε_{SP} [%]	m_{Hexane}	m_{Water}	$m_{o\text{-}Tolunitrile}$	$m_{o\text{-}Toluidine}$	$m_{m\text{-}Cresol}$	$m_{2,4\text{-}Xylenol}$	$m_{Solvent}$	ε_{HP} [%]
Solvent : Feed = 1.3; Hexane : Feed = 5.6; Water : Solvent = 5.0 (Molar Ratios)																	
s5a	TEG	0.496	6.032	0.352	0.640	0.000	3.286	10.131	2.4	24.254	0.013	0.652	0.367	0.000	0.670	0.022	1.4
s2a	DiEGD	0.334	6.209	0.415	0.747	0.000	3.609	18.032	2.6	22.929	0.008	0.591	0.282	0.000	0.399	0.000	0.6
s5b	Tetra EG	0.412	6.273	0.453	0.733	0.000	3.553	13.471	2.6	23.930	0.007	0.559	0.266	0.000	0.372	0.067	1.4
s5d	Tetraglyme	**Three Liquid Phases Formed**															
s5c	Glycerol	0.039	5.773	0.002	0.022	0.000	0.092	6.412	4.0	24.539	0.083	1.003	1.010	0.000	3.898	0.297	6.8
s5e	Methanol	0.195	23.995	0.017	0.129	0.000	0.346	7.585	3.7	98.211	0.000	3.990	3.974	0.000	15.847	1.220	2.7
Solvent : Feed = 0.9; Hexane : Feed = 5.4; Water : Solvent = 2.1 (Molar Ratios)																	
s6d	TEG	0.565	1.651	0.464	0.658	0.000	3.410	6.549	3.1	21.530	0.005	0.504	0.295	0.000	0.364	0.011	-0.8
s3a	DiEGD	0.063	1.711	0.454	0.696	0.000	3.468	11.653	1.2	22.886	0.005	0.502	0.235	0.000	0.318	0.000	3.6
s6c	Tetra EG	0.767	1.588	0.463	0.673	0.000	3.341	9.005	6.2	21.713	0.090	0.487	0.252	0.000	0.337	0.019	-4.2
s6b	Tetraglyme	**Three Liquid Phases Formed**															
s6a	Glycerol	0.315	1.640	0.002	0.018	0.000	0.072	3.900	2.3	22.758	0.061	0.931	0.921	0.000	3.714	0.003	1.2
s6e	Methanol	0.122	5.940	0.009	0.045	0.000	0.141	1.714	1.3	81.786	0.031	3.488	3.387	0.000	13.533	3.298	1.3
Solvent : Feed = 0.8; Hexane : Feed = 3.0; Water : Solvent = 7.5 (Molar Ratios)																	
s7b	TEG	**Three Liquid Phases Formed**															
s7a	DiEGD	0.971	6.810	0.524	0.754	0.000	4.157	13.065	3.3	15.618	0.014	0.496	0.266	0.000	0.512	0.017	2.6
s7d	Tetra EG	0.736	6.931	0.516	0.751	0.000	4.129	9.545	3.5	14.502	0.011	0.480	0.255	0.000	0.517	0.047	4.0
s7e	Tetraglyme	**Three Liquid Phases Formed**															
s7f	Methanol	0.525	33.945	0.025	0.157	0.000	0.501	3.859	1.7	81.157	0.000	5.105	4.984	0.000	24.507	4.248	1.3

A3 Batch Extraction Data for Synthetic Phenol Feed Stream

Table A3.1: Masses of Components Added to Separating Funnels at 313.15K

Exp. ID	Masses of Components In [g]								Masses of Resulting Phases [g]		ε_{MB}
	m_{hexane}	m_{water}	$m_{mesitylene}$	m_{EMP}	$m_{aniline}$	$m_{benzonitrile}$	m_{Phenol}	m_{TEG}	$m_{Solvent\ Phase}$	$m_{Hexane\ Phase}$	In/Out [%]
1A	44.965	5.035	1.358	1.005	1.010	1.041	10.657	15.026	31.971	45.341	-3.5
1B	24.772	8.239	2.244	1.641	1.651	1.662	17.579	24.771	54.861	26.708	-1.2
1C	12.689	8.460	2.259	1.675	1.689	1.708	18.019	25.338	56.993	13.882	-1.3
1D	75.001	15.529	1.358	1.026	1.091	1.032	10.647	22.813	49.427	77.760	-1.0
2A	74.085	5.021	1.393	1.021	1.013	1.026	10.644	15.017	31.849	77.925	0.5
2B	24.003	16.023	2.241	1.611	1.628	1.668	17.037	24.040	60.440	26.672	-1.3
2C	12.780	17.051	2.404	1.711	1.704	1.725	18.163	25.590	65.466	15.764	0.1
2D	44.950	10.040	1.362	1.004	1.019	1.026	10.657	15.017	36.834	45.966	-2.7
3A	15.048	10.006	2.688	2.016	2.003	2.001	21.301	15.024	53.097	15.287	-2.4
3B	12.056	24.022	2.221	1.613	1.605	1.621	17.017	36.026	79.201	14.351	-2.7
3C	12.058	32.030	2.233	1.605	1.635	1.828	17.093	48.054	101.202	14.686	-0.6
3D	13.024	52.151	2.435	1.750	1.728	1.746	18.451	78.055	153.037	14.821	-0.9
4A	45.066	5.043	1.353	1.017	1.007	1.029	10.660	7.502	24.939	45.575	-3.0
4B	45.014	15.023	1.367	1.010	1.018	1.068	10.676	22.560	48.812	47.281	-1.7
4C	45.022	20.086	1.362	1.018	1.064	1.040	10.688	30.036	58.402	47.128	-2.3
4D	45.000	30.018	1.370	1.013	1.051	1.078	10.654	45.048	88.591	42.517	-3.0
5A	23.927	2.641	2.246	1.615	1.636	1.626	17.024	24.006	48.906	24.620	-1.6
5B	14.749	3.264	2.721	1.958	1.986	1.948	20.737	29.444	57.888	14.989	-3.1
5C	45.170	2.480	1.365	1.010	1.002	1.038	10.648	22.518	37.705	45.731	-2.1
5D	75.061	1.671	1.372	1.007	1.041	1.040	10.632	15.030	28.570	76.673	-1.5
6A	47.996	0.871	1.343	1.007	0.999	1.039	11.207	7.699	21.546	49.797	-1.1
6B	44.842	1.646	1.347	1.012	1.031	1.034	10.657	15.051	29.326	46.288	-1.3
6C	45.289	3.384	1.363	1.021	1.030	1.021	10.716	30.014	45.447	46.602	-1.9
6D	44.893	5.008	1.348	1.049	1.021	1.003	10.670	45.071	60.992	45.993	-2.8
7A	75.200	5.048	1.360	1.005	1.040	1.064	10.807	7.528	23.889	78.106	-1.0
7B	75.201	10.018	1.355	1.007	1.025	1.012	10.876	15.015	36.172	78.252	-0.9
7C	75.130	20.039	1.364	1.013	1.032	1.013	10.755	30.457	61.753	77.725	-0.9
7D	76.000	30.205	1.361	1.068	1.049	1.023	10.652	45.094	86.235	78.654	-0.9
8A	30.066	10.038	2.714	2.021	2.010	2.011	21.477	15.007	51.425	34.785	1.0
8B	22.533	22.542	2.022	1.529	1.595	1.502	16.078	33.772	72.258	27.387	-1.9
8C	19.894	28.125	1.671	1.253	1.274	1.271	13.354	37.736	81.553	22.052	-0.9
8D	15.162	30.067	1.364	1.023	1.051	1.019	10.777	45.042	87.782	13.401	-3.1
8E	15.500	30.032	1.363	1.033	1.053	1.036	10.659	45.052	87.499	17.081	-1.1
9A	67.500	3.752	2.112	1.517	1.652	1.558	16.009	11.308	33.427	72.952	0.9
9B	45.502	7.615	1.448	1.012	1.048	1.027	10.672	22.521	42.366	47.623	-0.9
9C	45.270	10.274	1.386	1.025	1.006	1.007	10.344	30.115	52.488	47.246	-0.7
9D	45.084	15.218	1.364	1.034	1.029	1.012	10.726	45.070	72.845	45.818	-1.6
10A	22.535	11.392	2.053	1.542	1.587	1.572	16.101	33.831	65.307	24.102	-1.3
10B	15.066	2.600	1.362	1.114	1.096	1.050	10.643	7.699	23.954	15.802	-2.2
10C	14.980	10.074	1.371	1.045	1.017	1.021	10.744	30.110	53.071	16.122	-1.7
10D	15.848	15.050	1.506	1.072	1.081	1.019	11.079	45.088	73.652	15.646	-2.7
11A	11.269	11.392	2.013	1.521	1.542	1.525	16.005	33.847	65.748	11.430	-2.4
11B	11.466	3.797	2.026	1.527	1.529	1.553	16.083	11.300	36.595	11.748	-1.9
11C	11.294	15.094	2.072	1.502	1.560	1.525	16.055	45.053	80.531	12.521	-1.2
11D	11.329	22.585	2.067	1.504	1.547	1.520	16.087	67.633	110.639	10.614	-2.4

Table A3.1: Masses of Components Added to Separating Funnels at 313.15 K(cont.)

Exp. ID	Masses of Components In [g]								Masses of Resulting Phases [g]		ε_{MB}
	m_{hexane}	m_{water}	$m_{mesitylene}$	m_{EMP}	$m_{aniline}$	$m_{benzonitrile}$	m_{Phenol}	m_{TEG}	$m_{Solvent\ Phase}$	$m_{Hexane\ Phase}$	In/Out [%]
12A	24.441	4.098	2.180	1.627	1.706	1.621	17.222	36.748	63.178	25.420	-1.2
12B	22.618	5.139	2.016	1.531	1.571	1.673	16.083	45.228	71.205	23.490	-1.2
12C	22.666	1.372	2.051	1.501	1.505	1.531	16.050	11.622	34.028	23.346	-1.6
12D	15.303	5.185	1.374	1.029	1.001	1.046	10.693	45.121	64.069	15.472	-1.5
13A	80.100	2.882	1.391	1.028	1.125	1.177	10.651	8.272	22.382	82.667	-1.5
13B	75.301	7.568	1.372	1.033	1.060	1.051	10.672	22.670	41.994	77.712	-0.8
13C	75.000	10.085	1.392	1.014	1.055	1.013	10.692	30.080	52.061	77.304	-0.7
13D	75.400	15.017	1.414	1.020	1.025	1.018	10.677	45.205	72.006	76.925	-1.2
14A	75.702	0.964	1.367	1.019	1.014	1.034	10.708	7.632	20.191	78.057	-1.2
14B	75.300	2.518	1.360	1.035	1.012	1.077	10.747	22.610	37.450	77.181	-0.9
14C	75.303	3.340	1.359	1.037	1.020	1.046	10.740	30.056	45.668	76.874	-1.1
14D	75.699	5.023	1.366	1.003	1.044	1.026	10.841	46.006	63.899	76.847	-0.9
15A	88.900	0.000	1.686	1.199	1.209	1.187	12.733	18.052	32.818	90.873	-1.0
15B	75.502	0.000	1.352	1.053	1.019	1.038	10.713	22.832	35.604	76.629	-1.1
15C	75.911	0.000	1.364	1.040	1.057	1.049	10.765	30.051	43.174	76.878	-1.0
15D	75.800	0.000	1.405	1.026	1.032	1.005	10.721	46.880	60.313	76.181	-1.0
16A	45.900	0.000	1.361	1.097	1.014	1.010	10.656	22.688	36.100	46.667	-1.1
16B	46.302	0.000	1.360	1.011	1.074	1.025	10.750	30.107	43.872	46.803	-1.0
16C	45.701	0.000	1.363	1.029	1.064	1.075	10.669	45.102	59.095	45.815	-1.0
16D	50.400	0.000	1.506	1.122	1.123	1.103	12.006	16.928	31.844	51.213	-1.3
17A	45.602	18.110	1.366	1.020	1.025	1.014	10.788	45.100	75.545	47.196	-1.0
17B	45.703	27.116	1.352	1.058	1.026	1.015	10.806	47.700	86.890	48.396	-0.4
17C	45.502	12.021	1.367	1.025	1.031	1.045	10.749	30.100	54.430	47.392	-1.0
17D	45.900	19.115	1.379	1.089	1.013	1.015	10.646	31.384	62.472	46.575	-2.2
18A	49.101	5.510	1.024	1.472	2.011	2.227	9.630	16.397	34.812	50.585	-2.3
18B	47.805	5.379	1.043	1.987	0.525	0.498	11.794	15.800	33.956	50.093	-0.9
18C	47.409	5.651	1.001	1.363	0.522	1.013	11.795	15.803	34.675	49.324	-0.6
18D	45.899	5.014	1.044	1.409	2.003	0.954	9.695	15.513	32.893	47.579	-1.3
18E	48.689	5.425	1.369	1.069	1.002	1.024	11.692	16.800	35.545	50.745	-0.9
19A	47.301	6.036	1.380	1.020	1.016	1.018	10.952	16.077	34.602	47.398	-3.3
19B	45.811	9.054	1.362	1.047	1.001	1.034	11.078	15.201	36.504	47.844	-1.4
19C	45.500	7.787	1.012	0.753	0.773	0.767	8.073	23.068	40.399	46.583	-0.9
19D	47.400	5.439	1.019	0.784	0.828	0.874	8.094	15.921	30.254	48.477	-2.0
19E	35.101	2.912	1.922	1.240	1.275	1.219	12.682	9.029	27.099	36.764	-2.3

Table A3.2. Equilibrium Mass of Hexane(1), Water(2), Mesitylene(3), 5-Et-2-me-pyridine(4), Aniline(5), Benzonitrile(6), Phenol(7) and Triethylene Glycol(8) in Solvent and Antisolvent Phase for Batch Extractions using the Phenol Feed Stream at 313.15K

Exp.	Masses of Components in Solvent Phase [g]								ε_{SP}	Masses of Components in Antisolvent Phase [g]								ε_{HP}	Mass Balance Errors over Components [%]							
ID	m_1^I	m_2^I	m_3^I	m_4^I	m_5^I	m_6^I	m_7^I	m_8^I	[%]	m_1^{II}	m_2^{II}	m_3^{II}	m_4^{II}	m_5^{II}	m_6^{II}	m_7^{II}	m_8^{II}	[%]	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8
1A	0.360	4.938	0.058	0.484	0.862	0.662	9.911	15.068	1.2	41.314	0.019	1.275	0.546	0.145	0.392	0.639	0.148	-1.9	-1.2	-1.5	-1.8	2.5	-0.3	1.2	-1.0	1.3
1B	0.797	7.990	0.288	1.157	1.534	1.386	16.781	23.925	-1.8	23.049	0.014	1.915	0.477	0.105	0.313	0.534	0.033	-1.0	0.3	-2.9	-1.8	-0.4	-0.7	2.2	-1.5	-3.3
1C	0.872	8.404	0.509	1.324	1.600	1.559	17.468	25.960	1.2	10.972	0.005	1.559	0.321	0.065	0.195	0.357	0.014	-2.8	1.0	-0.6	-8.5	-1.8	-1.4	2.7	-1.1	2.5
1D	0.232	15.894	0.018	0.289	0.857	0.461	9.651	22.332	0.6	75.770	0.014	1.318	0.759	0.256	0.613	0.997	0.104	2.7	3.1	2.4	-1.6	2.2	1.9	4.1	0.0	-1.7
2A	0.394	5.041	0.039	0.344	0.820	0.552	9.768	15.126	0.7	72.748	0.025	1.323	0.655	0.195	0.457	0.802	0.005	-2.2	-2.0	0.9	-2.2	-2.2	0.2	-1.7	-0.7	0.8
2B	0.444	16.710	0.180	1.002	1.470	1.280	16.329	23.695	1.1	22.458	0.012	2.017	0.566	0.118	0.390	0.692	0.004	-1.6	0.2	3.4	-2.0	-2.7	-2.5	0.1	-0.1	-1.4
2C	0.567	16.790	0.362	1.188	1.562	1.443	17.369	25.500	-1.0	12.069	0.010	2.034	0.498	0.112	0.295	0.577	0.003	-1.1	-1.9	-1.5	-0.3	-1.5	-1.8	0.8	-1.2	-0.3
2D	0.241	9.914	0.044	0.397	0.820	0.575	9.740	14.886	-0.6	43.559	0.029	1.369	0.622	0.171	0.446	0.816	0.086	2.5	2.6	-1.0	3.7	1.5	-2.7	-0.5	-0.9	-0.3
3A	0.798	10.078	0.648	1.475	1.799	1.749	21.114	14.526	-1.7	11.969	0.013	1.976	0.501	0.138	0.276	0.750	0.005	2.2	-2.3	0.9	-2.4	-2.0	-3.3	1.2	2.6	-3.3
3B	0.307	24.272	0.259	1.127	1.485	1.327	16.602	35.915	2.6	11.151	0.009	1.902	0.493	0.104	0.308	0.517	0.006	1.0	-2.0	1.1	-2.7	0.4	-1.0	0.9	0.6	-0.3
3C	0.245	31.895	0.222	1.102	1.529	1.454	16.873	48.878	1.0	11.316	0.008	2.068	0.534	0.072	0.347	0.472	0.007	0.9	1.3	-0.4	2.6	1.9	-2.1	-1.5	1.5	1.7
3D	0.177	52.405	0.229	1.295	1.657	1.502	18.293	76.668	-0.5	11.727	0.009	2.200	0.493	0.052	0.280	0.368	0.009	2.1	3.1	0.5	-0.2	2.2	-1.1	2.1	1.1	-1.8
4A	0.258	5.112	0.053	0.402	0.835	0.607	9.620	7.540	-2.1	41.768	0.024	1.268	0.622	0.179	0.431	1.098	0.025	-0.4	-2.0	1.8	-2.4	0.7	0.7	0.9	0.5	0.8
4B	0.157	15.404	0.030	0.370	0.837	0.610	9.770	22.474	1.7	45.174	0.017	1.325	0.669	0.151	0.449	0.735	0.013	2.6	0.7	2.7	-0.9	2.9	-2.9	-0.8	-1.6	-0.3
4C	0.133	19.962	0.028	0.363	0.884	0.622	9.700	29.034	4.0	41.903	0.016	1.325	0.685	0.143	0.442	0.676	0.048	-4.0	-3.6	-0.5	-0.7	2.9	-3.5	2.3	-2.9	-3.2
4D	0.291	30.420	0.037	0.371	0.925	0.660	10.143	44.022	-1.9	40.790	0.013	1.330	0.611	0.119	0.436	0.504	0.015	3.1	0.5	1.4	-0.2	-3.1	-0.7	1.7	-0.1	-2.2
5A	0.301	2.743	0.456	1.177	1.519	1.382	16.575	23.523	-2.5	21.749	0.010	1.840	0.386	0.093	0.267	0.479	0.019	0.9	-3.0	2.3	2.2	-3.2	-1.5	1.4	0.2	-1.9
5B	0.307	3.333	0.875	1.649	1.888	1.773	19.633	27.308	-1.9	12.041	0.014	1.770	0.268	0.060	0.176	0.339	0.016	-2.0	1.6	2.5	-2.8	-2.1	-1.9	0.1	-3.7	-7.2
5C	0.422	2.552	0.105	0.551	0.866	0.714	10.094	22.645	0.6	44.118	0.015	1.215	0.479	0.108	0.320	0.486	0.032	2.3	-1.4	3.5	-3.3	2.0	-2.8	-0.4	-0.6	0.7
5D	0.575	1.668	0.055	0.393	0.816	0.591	9.920	14.759	0.7	75.169	0.017	1.314	0.607	0.218	0.475	0.918	0.057	2.7	3.1	0.8	-0.2	-0.7	-0.7	2.5	1.9	-1.4
6A	0.838	0.881	0.094	0.500	0.800	0.651	10.053	7.545	-0.9	45.866	0.011	1.233	0.485	0.173	0.381	1.065	0.034	-1.1	-1.0	2.4	-1.2	-2.2	-2.6	-0.7	-0.8	-1.6
6B	0.590	1.686	0.106	0.549	0.897	0.707	10.089	14.862	0.5	44.658	0.008	1.237	0.459	0.133	0.332	0.581	0.026	2.5	3.2	2.9	-0.3	-0.4	-0.1	0.5	0.1	-1.1
6C	0.496	3.304	0.131	0.569	0.917	0.698	10.644	29.626	2.1	43.421	0.006	1.207	0.470	0.118	0.324	0.452	0.026	-1.2	-3.0	-2.2	-1.8	1.8	0.5	0.1	3.5	-1.2
6D	0.612	5.008	0.160	0.646	0.943	0.745	10.530	44.740	3.9	43.797	0.008	1.197	0.384	0.070	0.239	0.238	0.002	-0.1	-1.1	0.2	0.7	-1.8	-0.8	-1.9	0.9	-0.7

Table A3.2. Equilibrium Mass of Hexane(1), Water(2), Mesitylene(3), 5-Et-2-me-pyridine(4), Aniline(5), Benzonitrile(6), Phenol(7) and Triethylene Glycol(8) in Solvent and Antisolvent Phase for Batch Extractions using the Phenol Feed Stream at 313.15K

Exp.	Masses of Components in Solvent Phase [g]								ε_{SP}	Masses of Components in Antisolvent Phase [g]								ε_{HP}	Mass Balance Errors over Components [%]							
ID	M_1^I	m_2^I	m_3^I	m_4^I	m_5^I	m_6^I	m_7^I	m_8^I	[%]	m_1^{II}	m_2^{II}	m_3^{II}	m_4^{II}	m_5^{II}	m_6^{II}	m_7^{II}	m_8^{II}	[%]	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8
7A	0.507	5.108	0.035	0.319	0.726	0.508	9.051	7.341	-1.2	73.672	0.019	1.343	0.692	0.295	0.582	1.459	0.043	0.0	0.0	1.6	1.3	0.6	-1.8	2.4	-2.7	-1.9
7B	0.353	10.037	0.025	0.275	0.768	0.446	9.588	15.001	0.9	74.011	0.018	1.339	0.730	0.244	0.559	1.057	0.017	-0.4	0.3	0.4	0.7	-0.2	-1.3	-0.7	-2.1	0.0
7C	0.405	20.173	0.020	0.285	0.819	0.457	9.739	29.939	0.1	73.886	0.014	1.347	0.719	0.227	0.568	0.892	0.015	-0.1	-1.1	0.7	0.2	-0.9	1.4	1.2	-1.2	-1.7
7D	0.331	30.654	0.032	0.328	0.881	0.504	9.907	45.593	2.3	76.861	0.010	1.291	0.716	0.178	0.528	0.640	0.023	2.0	1.6	1.5	-2.8	-2.2	1.0	0.9	-1.0	1.2
8A	0.995	10.184	0.344	1.353	1.796	1.544	19.821	14.858	-1.0	29.032	0.022	2.347	0.630	0.168	0.427	1.144	0.013	-2.9	-2.9	1.7	-0.8	-1.9	-2.3	-2.0	-2.4	-0.9
8B	0.430	21.940	0.138	0.911	1.470	1.142	15.276	32.982	2.8	22.872	0.010	1.876	0.634	0.120	0.378	0.660	0.012	-3.0	3.4	-2.6	-0.4	1.0	-0.3	1.2	-0.9	-2.3
8C	0.382	27.893	0.086	0.720	1.162	0.943	12.713	36.915	-0.9	19.264	0.006	1.555	0.517	0.086	0.323	0.495	0.012	0.9	-1.2	-0.8	-1.8	-1.3	-2.0	-0.4	-1.1	-2.1
8D	0.476	30.022	0.097	0.697	1.003	0.841	10.304	43.987	-0.4	11.298	0.005	1.244	0.343	0.046	0.205	0.263	0.007	0.1	-1.2	-0.1	-1.7	1.7	-0.2	2.6	-1.9	-2.3
8E	0.242	30.805	0.071	0.649	0.981	0.809	10.135	44.729	1.1	14.570	0.005	1.265	0.395	0.053	0.231	0.286	0.114	-1.0	-2.4	2.6	-2.0	1.1	-1.8	0.4	-2.2	-0.5
9A	1.045	3.804	0.115	0.746	1.341	0.996	14.423	10.945	0.0	66.611	0.022	1.969	0.750	0.265	0.585	1.516	0.048	-1.6	-1.2	2.0	-1.3	-1.4	-2.8	1.5	-0.4	-2.8
9B	0.401	7.817	0.062	0.489	0.925	0.664	9.820	22.079	-0.3	45.051	0.009	1.378	0.533	0.140	0.385	0.566	0.016	1.0	1.8	2.8	-0.6	1.0	1.6	2.1	-2.7	-1.9
9C	0.340	10.293	0.044	0.508	0.913	0.670	10.066	30.048	0.8	43.537	0.008	1.357	0.531	0.121	0.349	0.462	0.010	-1.8	-3.1	0.3	1.1	1.4	2.8	1.2	1.8	-0.2
9D	0.610	15.020	0.062	0.552	0.954	0.727	10.271	44.652	0.0	43.912	0.005	1.332	0.490	0.088	0.317	0.308	0.138	1.7	-1.2	-1.3	2.2	0.8	1.3	3.2	-1.4	-0.6
10A	0.642	11.726	0.243	1.082	1.461	1.332	15.451	33.504	0.2	21.148	0.006	1.757	0.439	0.087	0.285	0.416	0.024	0.2	2.2	3.0	-2.6	-1.4	-2.5	2.9	-1.5	-0.9
10B	0.496	2.657	0.242	0.802	0.972	0.871	9.933	7.591	-1.6	13.769	0.006	1.100	0.285	0.085	0.187	0.467	0.018	0.7	0.5	2.4	-1.5	-2.4	-3.6	0.8	-2.3	-1.2
10C	0.504	10.303	0.148	0.772	0.945	0.855	10.272	30.671	2.6	14.646	0.004	1.239	0.296	0.045	0.167	0.221	0.014	3.2	1.1	2.3	1.2	2.2	-2.7	0.1	-2.3	1.9
10D	0.327	15.004	0.174	0.803	1.009	0.863	10.702	45.186	0.6	13.950	0.003	1.313	0.271	0.035	0.151	0.168	0.011	1.6	-2.4	-0.3	-1.3	0.2	-3.4	-0.5	-1.9	0.2
11A	0.747	11.531	0.440	1.289	1.505	1.403	15.487	32.699	-1.0	9.542	0.003	1.599	0.261	0.045	0.157	0.239	0.004	3.7	-2.9	1.3	1.3	1.9	0.5	2.3	-1.7	-3.4
11B	0.569	3.905	0.627	1.285	1.497	1.441	15.534	11.664	-0.2	9.969	0.006	1.344	0.217	0.064	0.151	0.409	0.004	3.5	0.1	3.0	-2.7	-1.6	2.1	2.5	-0.9	3.3
11C	0.862	15.176	0.391	1.228	1.521	1.389	15.505	44.594	0.2	10.299	0.003	1.624	0.261	0.041	0.161	0.216	0.001	0.7	-1.2	0.6	-2.8	-0.9	0.1	1.6	-2.1	-1.0
11D	0.896	23.087	0.408	1.288	1.519	1.401	15.942	66.218	0.1	8.622	0.002	1.675	0.212	0.028	0.120	0.150	0.008	1.9	-3.1	2.2	0.8	-0.3	0.0	0.1	0.0	-2.1
12A	1.358	4.175	0.457	1.312	1.650	1.435	17.059	36.022	0.5	23.090	0.003	1.720	0.362	0.074	0.229	0.313	0.017	1.5	1.5	2.0	-0.1	2.9	1.1	2.6	0.9	-1.9
12B	0.840	5.200	0.429	1.228	1.551	1.527	15.462	44.893	-0.1	21.278	0.004	1.588	0.317	0.054	0.196	0.226	0.010	0.8	3.1	1.3	0.0	0.9	2.2	3.0	-2.5	-0.7
12C	1.594	1.392	0.419	1.173	1.394	1.298	14.947	11.324	-1.4	20.384	0.007	1.585	0.332	0.114	0.252	0.653	0.015	0.0	1.1	2.0	-2.3	0.3	0.2	1.2	-2.8	-2.4
12D	0.611	5.131	0.321	0.866	0.976	0.917	10.549	44.603	-0.1	14.418	0.002	1.071	0.197	0.025	0.107	0.113	0.008	3.0	2.3	-1.0	1.3	3.3	0.0	-2.1	-0.3	-1.1
13A	0.492	2.801	0.041	0.365	0.826	0.584	9.107	8.303	0.6	79.813	0.012	1.329	0.643	0.253	0.586	1.441	0.041	1.8	1.0	-2.4	-1.5	-1.9	-4.1	-0.6	-1.0	0.9
13B	0.445	7.566	0.031	0.385	0.858	0.559	9.877	22.186	-0.2	74.973	0.008	1.325	0.633	0.194	0.504	0.685	0.302	1.2	.1.5	0.1	-1.2	-1.5	-0.8	1.1	-1.0	-0.8
13C	0.422	9.989	0.036	0.395	0.882	0.549	9.996	29.710	-0.2	75.322	0.009	1.354	0.598	0.162	0.455	0.546	0.415	2.0	2.3	-0.9	-0.1	-2.1	-1.0	-0.9	-1.4	0.1

Table A3.2. Equilibrium Mass of Hexane(1), Water(2), Mesitylene(3), 5-Et-2-me-pyridine(4), Aniline(5), Benzonitrile(6), Phenol(7) and Triethylene Glycol(8) in Solvent and Antisolvent Phase for Batch Extractions using the Phenol Feed Stream at 313.15K (cont.)

Exp.	Masses of Components in Solvent Phase [g]								ε_{SP}	Masses of Components in Antisolvent Phase [g]								ε_{HP}	Mass Balance Errors over Components [%]							
ID	m_1^I	m_2^I	m_3^I	m_4^I	m_5^I	m_6^I	m_7^I	m_8^I	[%]	m_1^{II}	m_2^{II}	m_3^{II}	m_4^{II}	m_5^{II}	m_6^{II}	m_7^{II}	m_8^{II}	[%]	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8
13D	0.427	14.913	0.039	0.450	0.896	0.616	9.979	45.025	0.5	75.995	0.008	1.337	0.598	0.132	0.429	0.406	0.087	2.7	2.6	-0.6	-2.7	2.7	0.3	2.7	-2.7	-0.2
14A	0.829	0.974	0.050	0.397	0.744	0.538	9.115	7.555	0.1	74.905	0.015	1.328	0.620	0.272	0.504	1.392	0.076	1.4	0.6	2.6	0.8	-0.2	0.2	0.8	-1.9	0.0
14B	0.738	2.493	0.065	0.457	0.833	0.645	9.994	22.357	0.4	74.794	0.009	1.286	0.590	0.157	0.441	0.577	0.079	1.0	1.7	-0.6	-0.7	1.2	-2.2	0.8	-1.6	-0.8
14C	0.534	3.278	0.096	0.480	0.892	0.655	10.278	29.810	0.8	74.619	0.006	1.294	0.545	0.131	0.410	0.447	0.083	0.9	1.6	-1.7	2.3	-1.2	0.3	1.8	-0.1	-0.5
14D	0.663	4.899	0.126	0.528	0.942	0.697	10.358	45.149	-0.8	75.417	0.006	1.211	0.467	0.102	0.345	0.302	0.065	1.4	1.3	-2.3	-2.1	-0.8	0.0	1.6	-1.7	-1.7
15A	1.093	0.000	0.165	0.589	1.009	0.701	11.352	17.878	-0.1	86.556	0.000	1.552	0.627	0.200	0.504	0.989	0.083	-0.4	-0.9	0.0	1.8	1.4	0.0	1.5	-3.1	-0.5
15B	0.938	0.000	0.175	0.532	0.879	0.680	10.039	22.473	0.3	74.084	0.000	1.178	0.530	0.134	0.386	0.547	0.076	0.4	1.1	0.0	0.1	0.9	-0.6	2.7	-1.2	-1.2
15C	0.977	0.000	0.204	0.570	0.927	0.699	10.411	29.728	0.8	74.374	0.000	1.146	0.479	0.115	0.357	0.439	0.050	0.1	0.8	0.0	-1.0	0.9	-1.4	0.7	0.8	-0.9
15D	1.106	0.000	0.265	0.613	0.950	0.745	10.476	46.279	0.2	75.094	0.000	1.142	0.422	0.080	0.273	0.343	0.091	1.7	1.4	0.0	0.1	0.9	-0.2	1.3	0.9	-1.1
16A	1.248	0.000	0.179	0.651	0.918	0.749	10.056	22.337	0.1	44.597	0.000	1.195	0.440	0.086	0.277	0.411	0.049	0.8	0.6	0.0	1.0	-0.5	-1.0	1.6	-1.8	-1.3
16B	1.093	0.000	0.200	0.646	0.990	0.788	10.296	30.187	0.7	44.736	0.000	1.161	0.386	0.083	0.257	0.294	0.073	0.4	1.1	0.0	0.1	2.1	-0.1	2.0	-1.5	0.5
16C	1.141	0.000	0.285	0.691	0.995	0.891	10.429	44.830	0.3	43.708	0.000	1.076	0.348	0.055	0.211	0.201	0.058	-0.3	0.5	0.0	-0.1	1.0	-1.3	2.5	-0.4	-0.5
16D	1.483	0.000	0.162	0.665	0.963	0.749	11.297	16.886	1.1	48.304	0.000	1.336	0.447	0.143	0.342	0.740	0.051	0.3	-0.1	0.0	-0.5	-0.9	-1.5	-1.1	0.3	0.1
17A	0.224	18.055	0.036	0.495	0.930	0.648	10.129	44.461	-0.7	45.723	0.007	1.327	0.541	0.096	0.359	0.379	0.005	2.6	1.8	0.0	-0.2	1.6	0.1	-0.7	-2.6	-1.4
17B	0.127	26.979	0.025	0.443	0.910	0.642	10.484	46.674	-0.7	43.386	0.009	1.296	0.600	0.086	0.379	0.341	0.003	-2.7	-3.8	0.0	-2.3	-1.4	-2.9	0.6	0.2	-2.1
17C	0.199	12.029	0.038	0.449	0.929	0.641	10.584	29.517	-0.1	44.533	0.010	1.355	0.565	0.114	0.392	0.470	0.004	0.1	0.6	0.0	1.9	-1.1	1.2	-1.2	2.8	-1.9
17D	0.141	18.911	0.025	0.408	0.850	0.576	10.329	30.076	-0.1	44.266	0.012	1.358	0.687	0.132	0.449	0.602	0.001	2.0	-0.6	0.0	0.3	0.5	-3.1	0.9	2.7	-4.2
18A	0.454	5.469	0.041	0.653	1.697	1.245	8.699	16.233	-0.9	48.859	0.017	0.985	0.825	0.350	0.905	0.796	0.002	2.3	1.9	0.0	0.2	0.4	1.8	-3.5	-1.4	-1.0
18B	0.321	5.331	0.044	0.945	0.450	0.300	10.311	15.160	-3.2	44.668	0.012	1.004	1.129	0.088	0.187	1.158	0.002	-3.7	-2.3	0.0	0.5	4.4	2.6	-2.3	-2.8	-4.0
18C	0.416	5.621	0.041	0.658	0.448	0.642	10.554	15.892	-1.2	44.591	0.011	0.979	0.751	0.071	0.390	0.861	0.003	-3.4	-3.9	0.0	1.8	3.4	-0.7	1.9	-3.2	0.6
18D	0.381	5.029	0.042	0.644	1.689	0.560	9.122	15.028	-1.2	44.330	0.012	1.034	0.783	0.313	0.385	0.771	0.001	0.1	-0.3	1.0	3.0	1.3	-0.1	-1.0	2.0	-3.1
18E	0.432	5.438	0.055	0.501	0.843	0.615	10.545	16.552	-1.6	46.403	0.011	1.286	0.548	0.145	0.416	0.745	0.013	-2.3	-2.2	0.0	-2.1	-1.9	-1.4	0.7	-3.4	-1.4
19A	0.361	5.882	0.052	0.460	0.851	0.638	10.162	15.787	-1.6	45.557	0.010	1.350	0.560	0.146	0.399	0.626	0.030	2.7	-0.9	0.0	1.6	0.0	-1.9	1.9	-1.5	-1.6
19B	0.210	8.980	0.040	0.415	0.835	0.592	10.425	15.112	-1.6	45.647	0.014	1.309	0.662	0.183	0.423	0.792	0.060	2.6	2.9	0.0	-1.0	2.9	1.7	-1.8	1.3	-0.2
19C	0.319	7.787	0.027	0.303	0.663	0.463	7.687	23.099	-1.6	44.575	0.000	0.982	0.477	0.101	0.314	0.341	0.125	0.7	0.3	0.0	-0.3	3.6	-1.1	1.2	-0.6	0.7
19D	0.344	5.439	0.029	0.293	0.703	0.477	7.501	15.831	-1.6	45.318	0.000	0.986	0.499	0.133	0.385	0.455	0.045	-1.4	-0.2	0.0	-0.5	1.0	0.8	-1.3	-1.7	-0.3
19E	1.037	2.912	0.174	0.744	1.116	0.852	11.228	8.950	-1.6	33.619	0.000	1.782	0.506	0.169	0.345	0.937	0.092	1.9	0.9	0.0	1.8	0.8	0.7	-1.8	-4.1	0.1

A4 Batch Extraction Data for Synthetic m-Cresol Feed Stream

Table A4.1: Masses of Components Added to Separating Funnels at 313.15K

	Masses of Components In [g]									Masses of Resulting Phases [g]		ε_{MB} In/Out
Exp. ID.	m_{hexane}	m_{water}	$m_{pseudo-cumene}$	$m_{undecane}$	m_{indene}	$m_{o\text{-}tolunitrile}$	$m_{o\text{-}toluidine}$	$m_{m\text{-}cresol}$	m_{TEG}	$m_{Solvent\ Phase}$	$m_{Hexane\ Phase}$	[%]
c1a	45.600	5.174	1.032	1.002	3.267	1.068	1.022	8.022	7.648	21.438	50.352	-2.8
c1b	54.300	12.962	1.216	1.265	3.603	1.014	1.238	9.768	18.556	42.085	60.580	-1.2
c1c	45.600	15.503	1.009	1.009	3.003	1.028	1.042	8.069	22.627	46.850	50.931	-1.1
c1d	45.500	20.273	1.019	1.010	3.031	1.023	1.005	8.025	31.064	60.119	50.305	-1.4
c1e	45.100	30.094	1.054	1.005	3.013	1.084	1.361	8.184	45.482	84.778	49.564	-1.5
c2a	45.700	2.576	1.013	1.023	3.061	1.086	1.039	8.034	7.870	19.667	50.143	-2.2
c2b	48.000	6.006	1.475	1.339	3.057	1.472	1.270	10.530	17.457	35.784	53.665	-1.3
c2c	45.300	7.559	1.033	1.028	3.054	1.014	1.018	8.016	22.800	39.696	50.431	-0.8
c2d	46.000	10.061	1.016	1.027	3.025	1.063	1.033	8.040	32.597	52.119	50.340	-1.4
c2e	45.200	15.011	0.000	1.024	3.120	2.038	1.072	8.016	46.149	71.155	49.171	-1.1
c3a	45.900	5.153	1.011	1.022	3.039	1.023	1.015	8.010	15.031	29.277	50.679	-1.5
c3b	45.800	12.653	1.028	1.015	3.025	1.002	1.022	8.024	23.155	44.612	51.007	-1.1
c3c	7.575	10.017	1.029	1.030	3.038	1.021	1.052	8.013	15.538	35.945	11.935	-0.9
c3d	7.526	15.194	1.028	1.036	3.044	1.019	1.019	8.073	22.689	47.932	11.514	-1.9
c3e	7.498	22.402	1.019	1.008	3.129	1.030	1.030	8.028	30.055	62.167	11.440	-2.1
c4a	60.300	10.057	1.013	1.005	3.025	1.023	1.008	8.041	15.094	33.513	64.103	-2.9
c4b	60.400	5.196	1.018	1.015	3.075	1.025	1.018	8.018	7.510	20.742	66.413	-1.3
c4c	61.500	15.031	1.012	1.028	3.055	1.012	1.002	8.003	23.022	46.368	67.123	-1.0
c4d	60.100	20.223	1.043	1.003	3.059	1.007	1.023	8.020	31.800	60.440	64.264	-2.0
c4e	60.700	30.089	1.023	1.016	3.201	1.030	1.056	8.035	45.300	83.774	65.749	-1.3
c5a	61.400	2.692	1.011	1.009	3.017	1.017	1.023	8.020	7.675	19.136	64.669	-3.5
c5b	60.700	5.011	1.011	1.031	3.028	1.021	1.036	8.038	15.405	29.229	66.195	-0.9
c5c	60.600	7.518	1.013	1.013	3.013	1.009	1.010	8.031	23.115	39.547	65.609	-1.1
c5d	61.800	10.034	1.022	1.018	3.008	1.017	1.036	8.004	30.510	49.651	65.771	-1.7
c5e	61.000	15.032	1.019	1.004	3.002	1.005	1.017	8.025	45.003	69.065	63.884	-2.3
c6a	15.200	10.059	1.008	1.015	3.263	1.007	1.061	8.046	15.426	35.641	19.306	-2.0
c6b	45.100	1.670	1.020	1.002	3.668	1.016	1.004	8.069	15.072	27.020	50.142	-0.6
c6c	46.700	2.524	0.000	2.018	3.020	1.020	1.023	8.052	22.900	35.325	51.367	-0.6
c6d	45.600	3.782	0.000	2.042	3.170	1.036	1.072	8.054	30.300	44.291	49.817	-1.0
c6e	45.000	5.124	0.000	2.022	3.051	1.013	1.015	8.061	45.200	60.646	50.208	0.3
c7a	75.900	2.690	1.017	1.010	3.016	1.000	1.014	8.098	7.675	18.923	79.654	-2.8
c7b	75.800	5.022	1.002	1.014	3.049	1.013	1.005	8.038	15.405	28.998	81.698	-0.6
c7c	76.900	7.511	1.032	1.027	3.462	1.003	1.065	8.025	23.115	38.583	83.119	-1.2
c7d	76.000	10.118	1.009	1.004	3.026	1.010	1.018	8.012	30.510	49.645	79.372	-2.0
c7e	77.800	15.714	1.020	1.017	3.075	1.055	1.003	8.022	45.003	69.880	81.038	-1.8

Table A4.1: Masses of Components Added to Separating Funnels at 313.15K (cont.)

	Masses of Components In [g]									Masses of Resulting Phases [g]		ε_{MB} In/Out
Exp. ID.	m_{hexane}	m_{water}	$m_{pseudo\text{-}cumene}$	$m_{undecane}$	m_{indene}	$m_{o\text{-}tolunitrile}$	$m_{o\text{-}toluidine}$	$m_{m\text{-}cresol}$	m_{TEG}	$m_{Solvent\ Phase}$	$m_{Hexane\ Phase}$	[%]
c8a	75.100	5.011	1.013	1.001	3.032	1.014	1.024	8.009	7.548	20.298	80.964	-1.5
c8b	75.300	10.143	1.003	1.006	3.442	1.000	1.026	8.020	15.134	32.982	82.553	-0.5
c8c	76.100	15.461	1.008	1.006	3.019	1.015	1.018	8.016	22.700	46.580	82.602	-0.1
c8d	75.400	20.435	1.013	1.032	3.020	1.018	1.057	8.004	30.200	58.854	81.022	-0.9
c8e	75.400	30.143	1.004	1.005	3.046	1.001	1.004	8.024	45.200	83.613	80.852	-0.8
c9a	11.800	1.241	1.419	1.454	4.299	1.424	1.412	11.267	10.747	29.815	14.727	-1.2
c9b	7.800	1.675	1.013	1.000	3.020	1.028	1.026	8.009	15.023	28.917	10.225	-1.1
c9c	8.251	2.749	1.131	1.172	3.318	1.120	1.103	8.810	24.700	40.961	10.987	-0.8
c9d	7.600	3.386	1.015	1.006	3.021	1.009	1.045	8.011	30.000	45.634	9.828	-1.1
c9e	7.500	5.048	1.018	1.073	3.032	1.028	1.016	8.025	45.200	62.056	9.599	-1.8
c10a	75.000	0.856	1.014	1.011	3.110	1.014	1.030	8.009	7.560	17.267	81.043	-0.3
c10b	75.400	1.672	1.022	1.018	3.013	1.018	1.012	8.040	15.110	26.083	80.849	-0.3
c10c	76.600	2.504	1.016	1.008	3.045	0.999	1.031	8.073	22.900	35.142	81.980	0.0
c10d	75.500	3.367	1.021	0.998	3.038	1.012	1.021	8.018	30.100	43.097	79.882	-0.9
c10e	78.400	5.004	1.027	0.999	3.044	1.064	1.036	8.057	45.300	60.045	82.607	-0.9
c11a	53.300	0.000	1.162	1.194	3.501	1.192	1.160	9.262	8.713	20.203	58.670	-0.8
c11b	46.900	0.000	1.009	1.147	3.037	1.004	1.023	8.015	23.099	33.847	50.461	-1.1
c11c	45.100	0.000	1.011	1.024	3.022	1.045	1.005	8.021	15.200	26.035	48.644	-1.0
c11d	45.500	0.000	1.017	1.005	3.106	1.020	1.015	8.090	30.200	41.465	48.359	-1.2
c11e	45.200	0.000	1.011	1.013	3.030	1.029	1.073	8.010	45.125	56.644	46.905	-1.8
c12a	61.300	0.000	1.007	1.012	3.003	1.024	1.038	8.001	7.514	16.945	66.935	0.0
c12b	60.400	0.000	1.001	1.016	3.016	1.020	1.019	8.046	15.119	25.307	66.064	0.8
c12c	60.900	0.000	1.020	1.106	3.026	1.006	1.005	8.048	22.876	32.954	64.718	-1.3
c12d	60.300	0.000	1.008	1.016	3.039	1.010	1.009	8.042	30.000	40.406	63.563	-1.4
c12e	60.200	0.000	1.020	1.012	3.135	1.010	1.045	8.013	45.800	56.781	63.307	-0.9
c13a	76.300	0.000	1.003	1.011	3.025	1.018	1.015	8.024	7.613	16.520	81.954	-0.5
c13b	76.300	0.000	1.135	1.022	3.012	1.009	1.011	8.038	15.033	24.812	80.671	-1.0
c13c	75.100	0.000	1.003	1.022	3.021	1.032	1.019	8.093	22.568	33.035	79.069	-0.7
c13d	75.500	0.000	1.011	1.016	3.118	1.029	1.024	8.025	30.069	40.358	79.042	-1.2
c13e	75.000	0.000	1.020	1.012	3.033	1.014	1.014	8.064	45.245	56.722	78.096	-0.4
c14a	8.000	12.541	1.019	1.003	3.078	1.026	1.039	8.018	37.500	60.704	10.349	-3.0
c14b	15.400	12.540	1.020	1.005	3.026	1.020	1.002	8.020	37.500	60.075	20.193	-0.3
c14c	30.300	12.640	1.013	1.009	3.005	1.018	1.013	8.010	37.500	59.678	34.688	-1.2
c14d	45.500	12.538	1.015	1.005	3.008	1.005	1.038	8.075	37.500	59.879	48.896	-1.7
c14e	60.300	12.531	1.014	1.165	3.006	1.016	1.027	8.041	39.100	60.630	63.365	-2.5
c15a	75.000	0.000	1.067	1.005	3.052	1.024	1.013	8.040	37.988	48.699	78.262	-1.0
c15b	75.800	4.174	1.022	1.015	3.036	1.011	1.007	8.019	37.980	51.871	80.260	-0.7
c15c	76.100	12.522	1.021	1.003	3.033	1.003	1.011	8.016	38.722	60.369	81.914	-0.1
c15d	75.800	25.011	1.005	1.015	3.010	1.045	1.008	8.084	38.180	71.542	81.171	-0.9
c15e	75.000	37.735	1.002	1.016	3.042	1.006	1.039	8.053	38.111	83.859	81.172	-0.6

Table A4.1: Masses of Components Added to Separating Funnels at 313.15K (cont.)

	Masses of Components In [g]									Masses of Resulting Phases [g]		ε_{MB} In/Out
Exp. ID.	m_{hexane}	m_{water}	$m_{pseudo-cumene}$	$m_{undecane}$	m_{indene}	$m_{o\text{-}tolunitrile}$	$m_{o\text{-}toluidine}$	$m_{m\text{-}cresol}$	m_{TEG}	$m_{Solvent\ Phase}$	$m_{Hexane\ Phase}$	[%]
c16a	60.150	1.675	1.014	1.011	3.005	1.004	1.009	8.082	15.025	26.086	64.819	-1.2
c16b	61.636	2.508	1.015	1.018	3.034	1.014	1.027	8.010	22.695	34.881	65.946	-1.1
c16c	61.980	0.839	1.025	1.028	3.005	1.027	1.052	8.088	7.764	17.869	66.734	-1.4
c16d	61.169	3.339	1.008	1.018	3.037	1.009	1.049	8.016	30.598	43.742	64.830	-1.5
c16e	61.512	5.033	1.054	1.014	3.017	1.036	1.004	8.018	45.297	60.890	64.664	-1.1
c17a	46.067	0.839	1.010	1.018	3.049	1.018	1.003	8.055	7.622	17.981	50.681	-1.5
c17b	45.587	2.514	1.009	1.012	3.021	1.016	1.015	8.016	22.589	35.166	49.505	-1.3
c17c	45.205	3.340	1.026	1.010	3.019	1.012	1.015	8.038	30.449	44.584	48.709	-0.9
c17d	45.124	4.189	1.024	1.042	3.019	1.007	1.023	8.028	37.699	52.019	48.438	-1.7
c17e	45.435	5.033	1.024	1.014	3.052	1.027	1.010	8.005	45.109	60.691	50.001	0.0
c18a	76.432	0.000	1.270	1.301	3.846	1.289	1.278	10.247	47.700	61.503	80.536	-0.9
c18b	60.075	4.172	1.015	1.021	3.051	1.009	1.039	8.061	37.503	51.711	65.423	0.2
c18c	60.472	0.000	1.339	1.438	4.038	1.349	1.358	10.749	50.918	65.009	64.531	-1.6
c18d	60.480	25.101	1.005	1.019	3.039	1.005	1.021	8.084	37.936	71.496	63.515	-2.7
c18e	45.538	25.025	1.003	1.012	3.036	1.030	1.062	8.024	37.744	71.821	48.252	-2.8
c19a	7.503	5.005	1.016	1.010	3.008	1.015	1.014	8.017	15.140	31.340	9.552	-2.3
c19b	7.502	7.558	1.006	1.010	3.011	1.006	1.008	8.005	22.529	41.072	10.695	-1.6
c19c	7.597	10.007	1.001	1.001	3.042	1.004	1.015	8.037	30.069	50.876	10.822	-1.7
c19d	7.598	4.172	1.012	1.016	3.029	1.025	1.024	8.055	38.056	54.272	8.972	-2.7
c19e	7.603	15.849	1.018	1.002	3.014	1.026	1.011	8.023	44.970	74.855	7.178	-1.8
c20a	7.782	25.013	1.008	1.017	3.016	1.021	1.019	8.029	37.913	72.687	11.483	-1.9
c20b	7.689	30.000	1.018	1.011	3.012	1.026	1.027	8.010	45.463	86.679	12.415	0.9
c20c	15.651	15.429	1.015	1.012	3.011	1.011	1.014	8.015	45.448	71.007	19.485	-1.2
c20d	15.691	10.018	1.026	1.006	3.044	1.025	1.018	8.034	30.251	50.832	17.557	-3.8
c20e	15.869	7.693	1.010	1.012	3.102	1.027	1.016	8.018	22.852	41.046	18.788	-2.9
c21a	74.774	15.038	1.020	1.006	3.035	0.755	0.763	8.011	45.027	68.340	77.058	-2.7
c21b	76.070	15.031	1.014	1.012	3.046	0.612	0.615	8.091	45.088	68.460	79.669	-1.6
c21c	76.501	15.021	1.390	1.006	3.036	0.508	0.502	8.021	45.447	69.488	79.904	-1.3
c21d	60.674	15.455	1.031	0.999	3.012	0.864	0.772	8.061	45.039	69.766	62.199	-2.9
c21e	60.037	15.237	1.002	1.002	3.169	0.508	0.531	8.010	45.026	68.962	62.986	-1.9
c22a	60.360	10.056	1.001	1.083	3.035	0.774	0.753	8.017	30.159	48.900	63.713	-2.3
c22b	60.245	10.210	1.031	1.003	3.025	0.607	0.609	8.032	30.218	49.070	64.734	-1.0
c22c	86.252	10.008	1.012	1.016	3.032	0.831	0.782	8.029	30.265	49.141	90.678	-1.0
c22d	74.656	10.131	1.013	1.005	3.028	0.609	0.617	8.016	30.174	48.945	77.284	-2.3
c22e	79.606	10.191	1.014	1.014	3.061	0.519	0.519	8.006	30.444	48.879	82.564	-2.2

Table A4-2. :Equilibrium Masses of Hexane(1), Water(2), Pseudocumene(3), Undecane(4), Indene(5), o-tolunitrile(6), o-Toluidinel(7), m-Cresol(8) and Triethylene Glycol(9) in the Solvent and Antisolvent Phase for Batch Extractions using the m-Cresol Feed Stream at 313.15K

Exp.	Masses of Components in Solvent Phase [g]									ε_{SP}	Masses of Components in Antisolvent Phase [g]									ε_{HP}	Mass Balance Errors over Components [%]								
ID	m_1^I	m_2^I	m_3^I	m_4^I	m_5^I	m_6^I	m_7^I	m_8^I	m_9^I	[%]	m_1^{II}	m_2^{II}	m_3^{II}	m_4^{II}	m_5^{II}	m_6^{II}	m_7^{II}	m_8^{II}	m_9^{II}	[%]	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8	ε_9
c1a	0.503	5.224	0.038	0.0001	0.257	0.318	0.532	6.680	7.595	-1.4	43.977	0.026	1.014	1.018	3.023	0.748	0.475	1.422	0.281	3.2	2.1	1.5	1.9	1.6	0.4	-0.2	-1.5	1.0	3.0
c1b	0.494	12.853	0.056	0.0002	0.256	0.306	0.694	8.548	18.617	-0.6	52.185	0.017	1.154	1.261	3.371	0.719	0.540	1.210	0.304	0.3	-0.7	-0.7	-0.5	-0.3	0.7	1.1	-0.3	-0.1	2.0
c1c	0.339	15.156	0.017	0.0002	0.196	0.301	0.588	7.274	21.451	-3.3	43.959	0.013	0.976	1.031	2.842	0.723	0.455	0.949	0.834	1.7	-0.4	-2.2	-1.6	2.2	1.2	-0.4	0.1	1.9	-1.5
c1d	0.368	19.972	0.052	0.0003	0.199	0.328	0.658	7.535	31.089	0.1	43.432	0.010	0.978	1.000	2.859	0.694	0.350	0.512	0.206	-0.5	-0.4	-1.4	1.1	-0.9	0.9	-0.1	0.2	0.3	0.7
c1e	0.525	29.554	0.039	0.0004	0.264	0.365	0.955	7.736	45.600	0.3	42.310	0.009	1.015	0.999	2.781	0.712	0.397	0.313	0.538	-1.0	-0.5	-1.8	0.0	-0.5	1.1	-0.6	-0.7	-1.6	1.4
c2a	0.557	2.565	0.053	0.0068	0.331	0.409	0.576	6.985	7.669	-2.6	45.200	0.016	0.943	0.995	2.692	0.685	0.447	1.046	0.085	3.9	3.7	0.2	-1.7	-2.1	-1.2	0.7	-1.6	0.0	-1.5
c2b	0.813	5.892	0.088	0.0040	0.353	0.628	0.814	9.626	17.887	0.9	46.929	0.013	1.424	1.337	2.674	0.816	0.445	0.692	0.157	1.5	1.9	-1.7	2.5	0.1	-1.0	-1.9	-0.8	-2.0	3.4
c2c	0.330	7.606	0.041	0.0006	0.419	0.418	0.699	7.493	22.737	0.1	45.634	0.016	0.999	1.037	2.671	0.602	0.315	0.428	0.092	2.7	1.5	0.8	0.6	1.0	1.2	0.6	-0.4	-1.2	0.1
c2d	0.524	10.124	0.040	0.0049	0.341	0.445	0.760	7.681	32.228	0.1	45.096	0.006	0.970	1.039	2.636	0.609	0.276	0.302	0.184	1.5	2.3	0.7	-0.6	1.7	-1.6	-0.9	0.3	-0.7	-0.6
c2e	0.567	15.362	0.000	0.0069	0.410	0.954	0.831	7.653	46.274	1.3	44.405	0.007	0.054	1.022	2.762	1.118	0.251	0.178	0.070	1.4	2.5	2.4	0.0	0.5	1.7	1.7	0.9	-2.3	0.4
c3a	0.490	5.235	0.039	0.0029	0.330	0.400	0.665	7.330	14.706	-0.3	44.541	0.010	0.960	1.027	2.702	0.633	0.346	0.605	0.202	0.7	0.8	1.8	-1.2	0.8	-0.2	1.0	-0.4	-0.9	-0.8
c3b	0.377	12.728	0.033	0.0037	0.240	0.350	0.661	7.313	22.863	-0.1	44.178	0.013	0.969	1.038	2.785	0.630	0.360	0.584	0.163	-0.6	-0.3	0.7	-2.6	2.6	0.0	-2.2	-0.1	-1.6	-0.6
c3c	0.508	9.755	0.128	0.0126	0.802	0.553	0.825	7.461	15.426	-1.3	6.749	0.012	0.883	1.021	2.198	0.468	0.226	0.401	0.057	0.7	1.6	-2.5	-1.7	0.4	-1.2	0.0	-0.1	-1.9	-0.4
c3d	0.350	15.194	0.107	0.0058	0.759	0.553	0.813	7.567	22.365	-0.5	6.662	0.013	0.906	1.050	2.221	0.467	0.196	0.348	0.095	3.8	1.2	0.1	-1.4	1.9	-2.1	0.1	-1.0	-2.0	-1.0
c3e	0.504	22.840	0.081	0.0082	0.647	0.577	0.825	7.687	29.879	1.4	5.945	0.011	0.940	0.971	2.499	0.461	0.195	0.322	0.033	-0.5	0.0	2.0	0.0	-2.9	0.6	0.7	-1.0	-0.2	-0.5
c4a	0.332	9.999	0.030	0.0019	0.192	0.277	0.554	7.082	14.806	-0.7	58.349	0.019	0.963	0.984	2.827	0.739	0.457	0.922	0.154	2.0	2.3	-0.4	-2.0	-1.9	-0.2	-0.7	0.3	-0.5	-0.9
c4b	0.501	5.163	0.034	0.0023	0.222	0.279	0.495	6.575	7.377	-0.5	58.036	0.029	0.977	1.000	2.833	0.745	0.525	1.464	0.153	-1.0	-1.3	-0.1	-0.7	-1.2	-0.7	-0.1	0.2	0.3	0.3
c4c	0.363	14.937	0.017	0.0026	0.180	0.279	0.574	7.423	22.922	0.7	59.437	0.016	0.987	1.019	2.879	0.741	0.430	0.592	0.237	-1.2	-0.9	-0.5	-0.8	-0.6	0.2	0.8	0.2	0.1	0.6
c4d	0.389	19.752	0.014	0.0027	0.171	0.279	0.608	7.206	30.752	-2.1	59.029	0.014	1.026	0.996	2.906	0.735	0.404	0.575	0.117	2.4	-1.1	-2.3	-0.2	-0.4	0.6	0.7	-1.1	-3.0	-2.9
c4e	0.665	29.828	0.013	0.0022	0.176	0.292	0.683	7.330	46.297	1.8	59.444	0.013	1.028	1.007	3.035	0.744	0.373	0.476	0.075	0.7	2.3	-0.8	0.0	-0.7	0.3	0.6	0.0	-2.9	2.4
c5a	0.727	2.705	0.038	0.0043	0.304	0.345	0.554	6.778	7.409	-1.4	58.314	0.017	0.973	1.003	2.692	0.670	0.473	1.063	0.213	1.2	1.2	1.1	0.0	-0.1	-0.7	-0.2	0.4	-2.2	-0.7
c5b	0.522	5.007	0.035	0.0021	0.256	0.351	0.628	7.265	15.170	0.0	61.166	0.013	0.982	1.020	2.734	0.670	0.405	0.674	0.131	2.4	3.1	0.2	0.5	-0.8	-1.3	0.0	-0.3	-1.2	-0.7
c5c	0.429	7.399	0.029	0.0018	0.262	0.354	0.632	7.425	23.773	1.9	59.852	0.010	1.011	1.015	2.740	0.666	0.373	0.541	0.010	0.9	1.4	-1.4	2.7	0.4	-0.4	1.1	-0.5	-0.8	2.9
c5d	0.317	10.092	0.020	0.0007	0.279	0.368	0.721	7.617	30.262	0.1	57.174	0.010	1.003	1.031	2.749	0.650	0.318	0.380	0.122	-3.5	-3.8	0.7	0.1	1.3	0.7	0.1	0.3	-0.1	-0.4
c5e	0.171	15.084	0.032	0.0005	0.294	0.433	0.788	7.794	44.557	0.1	57.437	0.008	0.997	1.015	2.764	0.576	0.246	0.220	0.053	-0.9	-0.4	0.4	0.0	1.2	1.9	0.4	1.7	-0.1	-0.9

Table A4-2. :Equilibrium Masses of Hexane(1), Water(2), Pseudocumene(3), Undecane(4), Indene(5), o-tolunitrile(6), o-Toluidinel(7), m-Cresol(8) and Triethylene Glycol(9) in the Solvent and Antisolvent Phase for Batch Extractions using the m-Cresol Feed Stream at 313.15K (cont.)

Exp.	Masses of Components in Solvent Phase [g]									ε_{SP}	Masses of Components in Antisolvent Phase [g]									ε_{HP}	Mass Balance Errors over Components [%]								
ID	m_1^I	m_2^I	m_3^I	m_4^I	m_5^I	m_6^I	$m_7^{I'}$	m_8^I	m_9^I	[%]	m_1^{II}	m_2^{II}	m_3^{II}	m_4^{II}	m_5^{II}	m_6^{II}	m_7^{II}	m_8^{II}	m_9^{II}	[%]	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8	ε_9
c6a	0.583	9.997	0.075	0.0052	0.601	0.505	0.796	7.415	15.389	-0.8	13.848	0.004	0.939	1.009	2.663	0.502	0.257	0.440	0.023	2.0	2.6	-0.6	0.5	-0.1	0.0	0.0	-0.8	-2.4	-0.1
c6b	0.825	1.664	0.072	0.0078	0.543	0.464	0.709	7.522	15.325	0.4	43.449	0.007	0.967	0.983	3.177	0.556	0.283	0.400	0.044	-0.5	-0.8	0.1	1.9	-1.2	1.4	0.4	-1.2	-1.8	2.0
c6c	0.618	2.524	0.000	0.0150	0.577	0.513	0.800	7.716	22.401	-0.5	45.127	0.005	0.000	1.966	2.503	0.506	0.220	0.285	0.048	-1.4	-0.8	0.2	0.0	-1.8	2.0	-0.1	-0.3	-0.6	-2.0
c6d	0.573	3.765	0.000	0.0074	0.552	0.520	0.867	7.815	31.123	2.1	45.149	0.005	0.000	2.051	2.627	0.495	0.200	0.215	0.036	1.9	0.3	-0.3	0.0	0.8	0.3	-2.0	-0.5	-0.3	2.8
c6e	0.539	5.085	0.000	0.0187	0.756	0.587	0.857	7.669	43.695	-2.4	44.311	0.004	0.000	1.964	2.338	0.439	0.150	0.203	0.059	-1.5	-1.1	-0.7	0.0	-1.9	1.4	1.3	-0.7	-2.3	-3.2
c7a	0.981	2.697	0.028	0.0030	0.234	0.317	0.476	7.007	7.417	1.2	74.112	0.023	0.977	1.010	2.805	0.675	0.532	1.255	0.069	2.3	2.8	1.1	-1.2	0.3	0.8	-0.8	-0.6	2.0	-2.5
c7b	0.685	4.930	0.024	0.0012	0.228	0.310	0.584	7.536	15.376	2.3	75.339	0.013	0.970	1.022	2.861	0.713	0.419	0.712	0.016	0.4	1.2	-1.6	-0.8	0.9	1.3	1.0	-0.1	2.6	-0.1
c7c	0.555	7.273	0.028	0.0030	0.253	0.312	0.658	7.436	22.762	1.8	75.142	0.011	1.024	1.017	3.263	0.704	0.412	0.580	0.007	-1.2	0.3	-3.0	1.9	-0.7	1.6	1.3	0.5	-0.1	-1.5
c7d	0.551	9.979	0.027	0.0017	0.225	0.342	0.679	7.534	30.204	-0.2	74.491	0.010	0.999	1.026	2.809	0.686	0.350	0.453	0.058	1.9	2.4	-1.3	1.7	2.4	0.3	1.7	1.1	-0.3	-0.8
c7e	0.381	15.513	0.037	0.0020	0.260	0.352	0.693	7.683	44.713	-0.4	75.585	0.008	0.995	1.023	2.832	0.700	0.307	0.380	0.021	1.0	1.3	-1.2	0.0	0.8	0.6	-0.3	-0.3	0.5	-0.6
c8a	0.787	4.953	0.021	0.0018	0.169	0.240	0.444	6.692	7.332	1.7	72.993	0.015	0.983	0.986	2.833	0.782	0.584	1.430	0.075	-0.4	0.2	-0.9	-0.9	-1.3	-1.0	0.8	0.4	1.4	-1.9
c8b	0.536	9.994	0.009	0.0014	0.132	0.238	0.477	6.989	14.611	0.0	75.115	0.021	0.977	1.002	3.303	0.770	0.539	1.016	0.104	0.4	1.2	-1.3	-1.7	-0.2	-0.2	0.8	-0.9	-0.2	-2.8
c8c	0.411	15.232	0.013	0.0009	0.140	0.246	0.525	7.343	22.541	-0.3	74.027	0.082	0.994	0.994	2.860	0.788	0.484	0.861	0.014	-1.8	-2.0	-1.0	-0.1	-1.1	-0.6	1.9	-0.9	2.3	-0.6
c8d	0.255	20.187	0.013	0.0007	0.143	0.252	0.606	7.353	30.389	0.6	74.758	0.088	1.007	1.020	2.900	0.780	0.451	0.687	0.019	0.8	1.2	-0.8	0.7	-1.1	0.8	1.4	0.0	0.4	0.7
c8e	0.265	29.933	0.017	0.0012	0.172	0.256	0.621	7.361	45.001	0.0	73.808	0.081	0.975	1.006	2.924	0.762	0.398	0.571	0.052	-0.3	0.0	-0.4	0.0	0.2	1.6	1.6	1.5	-1.1	-0.3
c9a	2.025	1.252	0.477	0.1421	2.162	1.124	1.248	10.752	10.932	1.0	9.467	0.009	0.936	1.318	2.120	0.312	0.183	0.398	0.011	0.2	-2.6	1.6	-0.4	0.4	-0.4	0.8	1.3	-1.0	1.8
c9b	0.866	1.692	0.313	0.0504	1.465	0.824	0.940	7.894	15.757	3.1	6.923	0.003	0.692	0.931	1.524	0.214	0.095	0.129	0.005	2.8	-0.1	1.2	-0.8	-1.9	-1.0	0.9	0.8	0.2	4.9
c9c	1.119	2.806	0.327	0.0429	1.691	0.927	1.040	8.643	24.609	0.6	6.883	0.002	0.792	1.121	1.586	0.211	0.078	0.100	0.002	-1.9	2.0	2.1	-1.0	-0.7	-1.2	1.5	1.3	-0.8	-0.4
c9d	0.794	3.445	0.291	0.0390	1.618	0.854	1.003	7.878	30.257	1.2	6.657	0.002	0.734	0.976	1.411	0.172	0.061	0.072	0.036	3.0	-2.0	1.8	1.0	0.9	0.3	1.7	1.8	-0.8	1.0
c9e	0.838	5.027	0.316	0.0435	1.772	0.901	0.976	8.031	44.976	1.3	6.819	0.001	0.722	1.019	1.280	0.148	0.041	0.044	0.003	2.0	3.5	-0.4	0.0	-0.9	0.6	2.1	0.1	0.6	-0.5
c10a	1.505	0.846	0.045	0.0043	0.275	0.358	0.549	6.919	7.456	4.0	74.268	0.014	0.979	0.999	2.827	0.667	0.490	1.166	0.016	0.5	1.4	0.4	1.0	-0.7	-0.3	1.2	0.9	0.9	-1.2
c10b	0.690	1.669	0.044	0.0056	0.313	0.380	0.633	7.407	14.906	-0.1	73.014	0.007	0.958	1.011	2.729	0.620	0.373	0.620	0.018	-1.9	-1.8	0.2	-2.0	-0.1	1.0	-1.7	-0.6	-0.2	-1.2
c10c	0.666	2.565	0.046	0.0061	0.350	0.406	0.717	7.637	22.992	0.7	74.707	0.007	0.994	1.009	2.677	0.590	0.321	0.353	0.018	-1.6	-1.5	2.7	2.4	0.7	-0.6	-0.3	0.7	-1.0	0.5
c10d	0.700	3.362	0.040	0.0037	0.405	0.442	0.757	7.770	29.771	0.4	73.670	0.005	0.971	0.992	2.588	0.560	0.254	0.240	0.008	-0.7	0.0	0.0	-1.0	-0.2	-1.5	-1.0	-0.9	-0.1	-1.1
c10e	0.605	4.984	0.067	0.0079	0.512	0.512	0.810	7.887	45.293	1.1	74.751	0.005	0.958	0.994	2.540	0.544	0.220	0.176	0.023	-2.9	-2.3	-0.3	0.0	0.3	0.3	-0.8	-0.6	0.1	0.0

Table A4-2. :Equilibrium Masses of Hexane(1), Water(2), Pseudocumene(3), Undecane(4), Indene(5), o-tolunitrile(6), o-Toluidinel(7), m-Cresol(8) and Triethylene Glycol(9) in the Solvent and Antisolvent Phase for Batch Extractions using the m-Cresol Feed Stream at 313.15K (cont.)

Exp.	Masses of Components in Solvent Phase [g]									ε_{SP}	Masses of Components in Antisolvent Phase [g]									ε_{HP}	Mass Balance Errors over Components [%]								
ID	m_1^I	m_2^I	m_3^I	m_4^I	m_5^I	m_6^I	m_7^I	m_8^I	m_9^I	[%]	m_1^{II}	m_2^{II}	m_3^{II}	m_4^{II}	m_5^{II}	m_6^{II}	m_7^{II}	m_8^{II}	m_9^{II}	[%]	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8	ε_9
c11a	1.881	0.000	0.104	0.0237	0.635	0.530	0.748	8.291	8.571	2.9	52.484	0.000	1.057	1.181	2.814	0.651	0.421	0.899	0.028	1.5	3.2	0.0	-0.1	0.9	-1.5	-0.9	0.8	-0.8	-1.3
c11b	1.326	0.000	0.098	0.0170	0.780	0.562	0.808	7.700	22.599	0.1	44.430	0.000	0.905	1.139	2.284	0.442	0.220	0.211	0.009	-1.6	-0.5	0.0	-0.5	0.8	0.9	0.0	0.5	-1.3	-2.1
c11c	1.368	0.000	0.099	0.0157	0.702	0.581	0.793	7.737	15.425	2.6	43.019	0.000	0.919	1.016	2.345	0.455	0.211	0.193	0.019	-1.0	0.1	0.0	0.7	0.7	0.8	-0.9	-0.1	-1.1	1.6
c11d	1.338	0.000	0.124	0.0301	0.865	0.625	0.843	7.967	29.815	0.3	42.304	0.000	0.878	0.984	2.271	0.417	0.170	0.149	0.019	-2.4	-1.6	0.0	-1.4	0.9	1.0	2.2	-0.2	0.3	-1.2
c11e	1.254	0.000	0.156	0.0315	1.025	0.704	0.938	7.929	44.679	0.1	42.202	0.000	0.841	0.970	2.032	0.312	0.112	0.076	0.036	-0.7	0.5	0.0	0.0	-1.1	0.9	-1.2	-2.1	-0.1	-0.9
c12a	1.413	0.000	0.070	0.0134	0.416	0.390	0.611	7.075	7.549	3.5	58.936	0.000	0.933	0.993	2.582	0.628	0.434	0.945	0.050	-2.1	-1.5	0.0	-0.5	-0.5	-0.2	-0.6	0.7	0.2	1.1
c12b	1.357	0.000	0.070	0.0085	0.477	0.463	0.710	7.608	15.443	3.3	59.101	0.000	0.940	1.031	2.534	0.560	0.307	0.387	0.003	-1.8	-1.1	0.0	0.9	2.3	-0.2	0.3	-0.2	-0.6	2.2
c12c	1.494	0.000	0.074	0.0076	0.571	0.501	0.762	7.794	22.896	3.5	60.068	0.000	0.961	1.089	2.459	0.498	0.229	0.248	0.003	1.3	3.3	0.0	1.4	-0.9	0.1	-0.7	-1.4	-0.1	0.1
c12d	1.319	0.000	0.081	0.0097	0.635	0.532	0.801	7.796	29.807	1.4	59.998	0.000	0.939	0.998	2.390	0.495	0.212	0.197	0.003	2.6	1.7	0.0	1.1	-0.8	-0.4	1.7	0.4	-0.6	-0.6
c12e	2.010	0.000	0.100	0.0128	0.909	0.601	0.883	7.821	44.720	0.5	58.428	0.000	0.925	0.992	2.208	0.400	0.157	0.113	0.003	-0.1	2.3	0.0	0.0	-0.7	-0.6	-0.9	-0.5	-1.0	-2.4
c13a	1.357	0.000	0.055	0.0117	0.338	0.362	0.545	6.844	7.471	2.8	72.979	0.000	0.974	1.002	2.733	0.655	0.469	1.144	0.002	-2.4	-1.9	0.0	2.6	0.2	1.5	-0.1	-0.1	-0.5	-1.8
c13b	0.754	0.000	0.079	0.0129	0.382	0.447	0.684	7.381	15.136	0.3	75.672	0.000	1.069	1.004	2.665	0.554	0.317	0.498	0.003	1.4	1.6	0.0	1.1	-0.5	1.2	-0.8	-1.0	-2.0	0.7
c13c	1.369	0.000	0.081	0.0201	0.509	0.477	0.757	7.752	22.290	0.7	73.928	0.000	0.933	1.025	2.534	0.546	0.263	0.285	0.005	0.6	1.3	0.0	1.1	2.3	0.7	-0.9	0.1	-0.7	-1.2
c13d	1.767	0.000	0.077	0.0187	0.630	0.533	0.812	7.767	29.484	1.8	74.231	0.000	0.932	0.969	2.479	0.498	0.215	0.197	0.022	0.6	2.5	0.0	-0.2	-2.8	-0.3	0.2	0.3	-0.8	-1.9
c13e	1.181	0.000	0.246	0.1258	1.050	0.555	0.836	7.985	44.626	-0.2	73.731	0.000	0.779	0.914	1.982	0.459	0.179	0.144	0.017	0.1	0.7	0.0	0.0	2.8	0.0	0.0	0.1	0.8	-1.3
c14a	0.185	12.293	0.118	0.0036	1.120	0.724	0.935	8.095	36.924	-0.5	5.610	0.010	0.888	0.993	1.940	0.295	0.088	0.096	0.086	-3.3	-0.6	-1.9	-1.2	-0.7	-0.6	-0.7	-1.5	2.2	-1.3
c14b	0.243	12.436	0.076	0.0026	0.723	0.639	0.868	7.753	36.816	-0.9	15.127	0.012	0.944	1.015	2.316	0.378	0.129	0.114	0.039	-0.6	1.5	-0.7	0.0	1.2	0.4	-0.3	-0.5	-1.9	-1.7
c14c	0.201	12.532	0.068	0.0015	0.469	0.518	0.826	7.749	36.939	-0.6	28.838	0.009	0.946	1.003	2.493	0.480	0.182	0.153	0.006	-1.7	-0.4	-0.8	0.1	-0.4	-1.4	-2.0	-0.6	-1.3	-1.5
c14d	1.277	12.575	0.043	0.0020	0.380	0.445	0.791	7.723	37.227	1.0	42.002	0.005	0.975	1.011	2.666	0.544	0.250	0.186	0.379	-1.8	-0.7	0.3	0.3	0.8	1.3	-1.6	0.3	-2.1	0.3
c14e	1.358	12.278	0.042	0.0036	0.366	0.438	0.756	7.636	38.466	1.2	59.077	0.005	0.958	1.155	2.625	0.586	0.253	0.235	0.015	2.4	4.1	-2.0	0.0	-0.6	-0.5	0.8	-1.7	-2.1	-1.6
c15a	1.813	0.000	0.144	0.0477	0.738	0.557	0.837	7.776	37.818	2.1	71.904	0.007	0.920	0.954	2.322	0.466	0.181	0.150	0.015	-1.7	-0.1	0.0	-0.3	-0.3	0.3	-0.1	0.5	-1.4	-0.4
c15b	2.417	4.098	0.094	0.0138	0.548	0.448	0.748	7.905	37.378	3.4	76.495	0.005	0.933	0.997	2.495	0.551	0.242	0.212	0.018	2.1	4.4	-1.7	0.5	-0.4	0.2	-1.3	-1.7	1.2	-1.5
c15c	1.948	12.496	0.052	0.0031	0.308	0.366	0.702	7.613	37.519	1.1	75.142	0.010	0.961	0.984	2.712	0.645	0.313	0.380	0.020	-0.9	1.5	-0.1	-0.8	-1.6	-0.4	0.8	0.4	-0.3	-3.1
c15d	1.337	24.610	0.016	0.0022	0.143	0.263	0.579	7.493	37.065	0.0	73.461	0.009	1.013	1.026	2.918	0.786	0.415	0.653	0.013	-1.1	0.6	-1.6	2.4	1.3	1.7	0.4	-1.4	0.8	-2.9
c15e	0.465	37.133	0.006	0.0008	0.081	0.199	0.551	7.310	38.768	0.8	71.766	0.012	0.995	1.019	2.964	0.808	0.480	0.701	0.012	-3.0	-2.4	-1.6	0.0	0.4	0.1	0.1	-0.8	-0.5	1.8

Table A4-2. :Equilibrium Masses of Hexane(1), Water(2), Pseudocumene(3), Undecane(4), Indene(5), o-tolunitrile(6), o-Toluidinel(7), m-Cresol(8) and Triethylene Glycol(9) in the Solvent and Antisolvent Phase for Batch Extractions using the m-Cresol Feed Stream at 313.15K (cont.)

Exp.	Masses of Components in Solvent Phase [g]									ε_{SP}	Masses of Components in Antisolvent Phase [g]									ε_{HP}	Mass Balance Errors over Components [%]								
ID	m_1^I	m_2^I	m_3^I	m_4^I	m_5^I	m_6^I	m_7^I	m_8^I	m_9^I	[%]	m_1^{II}	m_2^{II}	m_3^{II}	m_4^{II}	m_5^{II}	m_6^{II}	m_7^{II}	m_8^{II}	m_9^{II}	[%]	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8	ε_9
c16a	0.668	1.735	0.045	0.0045	0.339	0.385	0.664	7.511	14.944	0.8	58.919	0.007	0.957	1.001	2.678	0.612	0.330	0.498	0.010	0.3	0.9	4.0	-1.2	-0.5	0.4	-0.7	-1.5	-0.9	-0.5
c16b	1.574	2.529	0.048	0.0044	0.454	0.443	0.744	7.753	22.304	2.8	58.916	0.006	0.956	1.006	2.578	0.567	0.276	0.268	0.010	-2.1	0.0	1.1	-1.1	-0.8	-0.1	-0.5	-0.7	0.1	-1.7
c16c	0.879	0.849	0.051	0.0073	0.357	0.382	0.589	7.191	7.795	1.3	58.821	0.013	0.974	1.008	2.688	0.650	0.451	0.978	0.013	-1.7	-1.8	2.7	0.0	-1.2	1.3	0.5	-1.2	1.0	0.6
c16d	1.059	3.368	0.052	0.0040	0.511	0.488	0.816	7.687	30.478	1.6	59.105	0.006	0.975	1.016	2.491	0.538	0.235	0.201	0.015	-0.4	1.1	1.0	1.9	0.2	-1.1	1.7	0.2	-1.6	-0.3
c16e	2.285	5.084	0.070	0.0087	0.575	0.550	0.810	7.859	45.588	3.2	57.953	0.004	1.006	1.020	2.424	0.498	0.176	0.126	0.016	-2.2	0.3	1.1	0.0	1.5	-0.6	1.2	-1.7	-0.4	0.7
c17a	0.575	1.241	0.075	0.0076	0.514	0.451	0.706	7.119	7.489	1.1	44.975	0.008	0.929	1.029	2.520	0.555	0.278	0.715	0.044	0.7	1.1	0.0	-0.5	1.8	-0.5	-1.2	-1.9	-2.7	-1.2
c17b	1.299	2.550	0.081	0.0168	0.550	0.523	0.778	7.762	22.590	2.8	43.183	0.004	0.940	0.981	2.473	0.493	0.246	0.256	0.011	-1.9	0.0	1.6	1.2	-1.4	0.1	0.0	0.9	0.0	0.1
c17c	1.355	3.366	0.106	0.0258	0.671	0.555	0.793	7.892	29.699	-0.3	44.513	0.004	0.917	0.995	2.349	0.461	0.207	0.187	0.032	2.0	1.5	0.9	-0.3	1.1	0.0	0.4	-1.5	0.5	-2.4
c17d	1.033	4.292	0.106	0.0215	0.725	0.574	0.849	7.889	37.048	1.0	42.830	0.003	0.925	1.018	2.317	0.443	0.166	0.129	0.010	-1.2	1.0	2.5	0.7	-0.3	0.8	1.0	-0.8	-0.1	-1.7
c17e	1.317	5.037	0.137	0.0265	0.735	0.594	0.853	8.077	44.991	1.8	43.190	0.002	0.897	0.989	2.339	0.434	0.152	0.108	0.008	-3.8	-2.0	0.1	0.0	0.2	0.7	0.1	-0.5	2.2	-0.2
c18a	1.111	0.000	0.163	0.0519	0.990	0.752	1.049	10.073	46.965	-0.6	74.646	0.002	1.073	1.242	2.841	0.531	0.224	0.189	0.001	0.3	0.9	0.0	-2.7	-0.5	-0.4	-0.5	-0.4	0.2	-1.5
c18b	0.771	4.189	0.098	0.0246	0.593	0.532	0.831	7.880	37.493	1.4	60.326	0.003	0.912	1.003	2.412	0.490	0.203	0.158	0.018	0.2	1.4	0.5	-0.5	0.6	-1.5	1.3	-0.6	-0.3	0.0
c18c	1.706	0.000	0.227	0.0957	1.343	0.901	1.180	10.704	50.947	3.2	58.990	0.002	1.098	1.361	2.697	0.473	0.184	0.141	0.015	0.7	4.0	0.0	-1.0	1.3	0.0	1.8	0.4	0.9	0.1
c18d	0.709	24.630	0.018	0.0031	0.169	0.279	0.645	7.548	37.428	-0.1	57.372	0.009	0.995	1.024	2.918	0.726	0.373	0.517	0.012	0.7	2.3	-1.8	0.8	0.8	1.6	0.0	-0.3	-0.2	-1.3
c18e	0.834	24.994	0.023	0.0032	0.237	0.341	0.743	7.890	37.808	1.5	43.027	0.009	0.969	1.016	2.808	0.700	0.322	0.359	0.018	2.0	4.1	-0.1	0.0	0.7	0.3	1.0	0.3	2.8	0.2
c19a	0.976	4.873	0.256	0.0386	1.100	0.697	0.878	7.982	15.027	1.6	5.400	0.004	0.753	0.990	1.930	0.302	0.129	0.192	0.006	1.6	-1.9	-2.6	-0.7	1.9	0.7	-1.5	-0.7	2.0	-0.7
c19b	0.388	7.516	0.178	0.0195	1.112	0.712	0.877	7.801	22.434	-0.1	6.361	0.003	0.824	0.976	1.914	0.296	0.115	0.135	0.003	-0.6	1.7	-0.5	-0.3	-1.5	0.5	0.2	-1.6	-0.9	-0.4
c19c	0.365	9.972	0.161	0.0167	1.111	0.723	0.907	7.919	30.856	2.3	6.602	0.002	0.822	0.975	1.917	0.299	0.096	0.109	0.003	0.0	2.5	-0.3	-1.8	-0.9	-0.5	1.8	-1.2	-0.1	2.6
c19d	0.752	4.233	0.270	0.0392	1.808	0.885	0.985	7.904	38.587	2.2	5.728	0.004	0.735	0.953	1.306	0.154	0.042	0.047	0.004	0.0	1.3	1.6	-0.7	-2.3	2.8	1.4	0.2	-1.3	1.4
c19e	1.833	15.645	0.228	0.0295	1.614	0.824	0.978	7.967	44.179	-2.1	3.908	0.002	0.828	0.956	1.413	0.214	0.047	0.046	0.003	3.3	-4.4	-1.3	0.0	-1.7	0.4	1.2	1.4	-0.1	-1.8
c20a	0.203	24.532	0.163	0.0087	0.764	0.578	0.854	8.035	37.806	0.4	6.649	0.006	0.857	1.037	2.212	0.457	0.157	0.224	0.005	1.1	2.3	-1.9	1.2	2.8	-1.3	1.5	-0.8	2.9	-0.3
c20b	0.223	30.814	0.063	0.0072	0.652	0.571	0.854	7.778	45.353	-0.4	7.149	0.005	0.939	1.016	2.339	0.451	0.155	0.211	0.009	-1.1	-3.0	2.7	-1.6	1.2	-0.7	-0.4	-1.7	-0.3	-0.2
c20c	0.282	15.409	0.103	0.0097	0.845	0.652	0.878	7.903	44.385	-0.8	15.425	0.003	0.918	1.004	2.216	0.363	0.124	0.094	0.016	3.5	-4.4	-0.1	0.6	0.2	1.7	0.5	-1.2	-0.2	-2.3

Table A4-2. :Equilibrium Masses of Hexane(1), Water(2), Pseudocumene(3), Undecane(4), Indene(5), o-tolunitrile(6), o-Toluidinel(7), m-Cresol(8) and Triethylene Glycol(9) in the Solvent and Antisolvent Phase for Batch Extractions using the m-Cresol Feed Stream at 313.15K (cont.)

Exp	Masses of Components in Solvent Phase [g]									ε_{SP}	Masses of Components in Antisolvent Phase [g]									ε_{HP}	Mass Balance Errors over Components [%]								
ID	m_1^I	m_2^I	m_3^I	m_4^I	m_5^I	m_6^I	m_7^I	m_8^I	m_9^I	[%]	m_1^{II}	m_2^{II}	m_3^{II}	m_4^{II}	m_5^{II}	m_6^{II}	m_7^{II}	m_8^{II}	m_9^{II}	[%]	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8	ε_9
c20d	0.664	10.014	0.094	0.0111	0.815	0.637	0.871	8.008	29.574	-0.3	13.407	0.004	0.940	0.991	2.214	0.388	0.145	0.163	0.002	4.0	-4.4	0.0	0.8	-0.4	-0.5	0.0	-0.2	1.7	-2.2
c20e	0.953	7.470	0.100	0.0137	0.778	0.623	0.836	7.931	22.863	1.3	13.854	0.005	0.917	0.978	2.346	0.410	0.181	0.216	0.001	0.6	-4.2	-2.8	0.7	-2.0	0.7	0.6	0.1	1.6	0.1
c21a	0.708	14.761	0.043	0.0052	0.336	0.262	0.523	7.802	45.517	2.4	72.484	0.005	1.001	1.016	2.764	0.491	0.241	0.220	0.002	1.5	3.5	-1.8	2.4	1.5	2.2	-0.3	0.2	0.1	1.1
c21b	0.745	14.616	0.069	0.0072	0.438	0.237	0.462	7.872	44.408	0.6	72.269	0.009	0.954	1.025	2.632	0.396	0.150	0.212	0.003	-2.5	-0.8	-2.7	0.9	2.0	0.8	3.5	-0.5	-0.1	-1.5
c21c	0.472	14.801	0.089	0.0095	0.441	0.181	0.384	7.785	45.533	0.3	73.782	0.010	1.303	1.025	2.626	0.331	0.121	0.225	0.003	-0.6	-0.3	-1.4	0.1	2.8	1.0	0.7	0.8	-0.1	0.2
c21d	0.272	15.488	0.053	0.0055	0.381	0.342	0.601	7.886	45.436	1.0	58.298	0.005	0.991	1.019	2.647	0.528	0.186	0.204	0.010	2.7	3.2	0.2	1.2	2.6	0.5	0.8	1.8	0.4	0.9
c21e	0.342	14.965	0.060	0.0079	0.510	0.232	0.487	7.966	45.830	2.1	56.700	0.005	0.969	0.983	2.613	0.286	0.049	0.176	0.003	-1.9	-0.7	-1.8	0.0	-1.2	-1.4	1.9	0.9	1.6	1.8
c22a	0.106	9.780	0.040	0.0056	0.324	0.280	0.539	7.753	30.702	1.3	60.012	0.006	0.961	1.080	2.696	0.508	0.210	0.278	0.004	3.2	-0.4	-2.7	0.0	0.2	-0.5	1.8	-0.4	0.2	1.8
c22b	0.188	10.059	0.048	0.0116	0.302	0.215	0.385	7.767	30.471	0.8	58.666	0.007	0.982	1.010	2.726	0.398	0.218	0.276	0.004	-0.7	-0.4	-1.4	-0.1	1.8	0.1	0.8	-1.1	0.1	0.9
c22c	0.221	9.730	0.045	0.0071	0.281	0.263	0.475	7.628	30.728	0.5	84.013	0.009	0.980	0.999	2.744	0.600	0.313	0.368	0.008	-0.7	-0.7	-2.7	1.2	-1.0	-0.2	3.9	0.8	-0.4	1.6
c22d	0.784	10.058	0.049	0.0061	0.295	0.197	0.386	7.764	30.047	1.3	72.229	0.009	0.961	1.002	2.761	0.422	0.228	0.317	0.008	0.8	1.9	-0.6	-0.3	0.3	0.9	1.7	-0.5	0.8	-0.4

A5 Batch Extraction Data for Synthetic Xylenol Feed Stream

Table A5.1: Masses of Components Added to Separating Funnels at 313.15K

Exp. ID.	Masses of Components In [g]									Masses of ResultingPhases [g]		ε_{MB} In/Out [%]
	m_{Hexane}	m_{Water}	m_{Indane}	$m_{Dode-cane}$	$m_{Naphtha-lene}$	$m_{2,4-Xylenol}$	$m_{3,5-Xylenol}$	$m_{3,4-Xylenol}$	m_{TEG}	$m_{Solvent\ Phase}$	$m_{Hexane\ Phase}$	
X1a	15.205	5.047	1.042	4.017	6.016	2.037	1.052	1.026	7.561	16.144	25.341	-3.5
x1b	30.413	20.073	2.046	8.026	12.056	4.018	2.008	2.053	30.028	56.814	52.283	-1.5
x1c	15.381	15.032	1.100	4.045	6.073	2.017	1.010	1.038	22.697	41.412	25.911	-1.6
x1d	15.800	20.069	1.071	4.025	6.004	2.061	1.032	1.008	30.042	53.854	26.122	-1.4
x1e	15.300	30.411	1.024	4.053	6.039	2.054	1.030	1.006	45.026	78.937	25.799	-1.1
x2a	75.100	5.020	1.013	4.009	6.089	2.004	1.032	1.004	7.522	14.927	85.847	-2.0
x2b	75.200	10.057	1.017	4.015	6.063	2.024	1.010	1.007	15.208	27.935	86.627	-0.9
x2c	75.400	15.157	1.047	4.021	6.039	2.024	1.033	1.000	22.558	40.509	86.757	-0.8
x2d	75.000	20.244	1.024	4.047	6.031	2.033	1.038	1.020	30.066	53.152	85.035	-1.6
x2e	75.500	30.071	1.027	4.136	6.025	2.025	1.019	1.004	45.389	78.430	85.538	-1.3
x3a	45.400	5.015	1.017	4.019	6.045	2.001	1.004	1.003	7.501	15.523	54.941	-3.5
x3b	45.200	10.041	1.022	4.021	6.013	2.003	1.017	1.054	15.055	28.243	56.184	-1.2
x3c	45.000	15.104	1.027	4.006	6.086	2.001	1.014	1.019	22.724	39.750	55.953	-2.3
x3d	45.100	20.288	1.019	4.034	6.002	2.149	1.013	1.009	30.137	53.873	55.696	-1.1
x3e	45.600	30.005	1.021	4.014	6.021	2.045	1.002	1.012	45.135	78.439	55.558	-1.4
x4a	59.900	7.568	1.001	4.013	6.092	2.024	1.003	1.046	7.519	17.177	69.990	-3.3
x4b	80.300	13.413	1.305	5.248	7.868	2.708	1.354	1.401	20.014	37.414	95.068	-0.8
x4c	60.200	15.041	1.013	4.231	6.015	2.032	1.021	1.019	22.569	40.788	69.934	-2.1
x4d	60.100	20.217	1.013	4.040	6.026	2.029	1.011	1.000	30.133	53.860	66.872	-3.9
x4e	60.500	27.330	1.027	4.256	6.062	2.046	1.047	1.007	45.287	74.953	71.922	-1.1
x5a	60.600	4.950	1.041	4.024	5.997	2.053	1.046	1.018	7.512	15.339	69.853	-3.5
x5b	60.900	5.014	1.064	4.017	6.082	2.026	1.021	1.017	15.148	23.736	72.504	-0.1
x5c	60.600	7.510	1.009	4.024	6.050	2.009	1.016	1.116	22.575	33.540	70.922	-1.4
x5d	60.200	10.033	1.011	4.009	6.072	2.001	1.036	1.039	30.005	43.858	67.259	-3.7
x5e	60.700	15.074	1.016	4.085	6.102	2.008	1.004	1.014	45.192	63.768	69.198	-2.4
x6a	45.600	5.304	1.013	4.088	6.042	2.014	1.003	1.039	15.578	24.425	55.344	-2.3
x6b	45.000	2.527	1.025	4.022	6.036	2.025	1.008	1.040	7.757	14.339	53.431	-3.8
x6c	45.500	7.535	1.025	4.024	6.010	2.028	1.021	1.041	22.500	33.846	55.547	-1.4
x6d	49.600	11.054	1.125	4.416	6.712	2.012	1.192	1.103	33.147	48.313	59.125	-2.6
x6e	45.100	15.028	1.017	4.052	6.044	2.036	1.032	1.038	45.409	64.366	53.826	-2.1
x7a	75.700	2.575	1.008	4.034	6.036	2.026	1.013	1.018	7.623	13.348	84.432	-3.2
x7b	75.600	5.015	1.019	4.031	6.144	2.024	1.056	1.015	25.129	34.085	85.681	-1.0
x7c	75.100	7.695	1.003	4.033	6.095	2.017	1.013	1.005	22.555	34.201	85.032	-1.1
x7d	60.600	30.016	1.011	4.126	6.035	2.030	1.005	1.017	45.532	78.707	70.613	-1.4
x7e	75.100	15.001	1.014	4.080	6.142	2.006	1.021	1.025	45.283	64.435	84.318	-1.3
x8a	60.200	2.540	1.010	4.038	6.136	2.032	1.014	1.014	7.595	13.432	70.008	-2.5
x8b	75.600	5.120	1.017	4.009	6.032	2.022	1.062	1.028	15.080	23.417	86.239	-1.2
x8c	22.700	11.292	1.502	6.007	9.041	3.028	1.536	1.558	34.144	52.626	36.919	-1.4
x8d	84.900	11.414	1.144	4.494	6.760	2.259	1.141	1.130	33.845	49.006	96.057	-1.4
x8e	22.700	22.607	1.518	6.102	9.173	3.073	1.529	1.512	67.510	97.184	37.239	-1.0

Table A5.1: Masses of Components Added to Separating Funnels at 313.15K

Exp. ID.	Masses of Components In [g]									Masses of ResultingPhases [g]		ε_{MB} In/Out [%]
	m_{Hexane}	m_{Water}	m_{Indane}	$m_{Dode-cane}$	$m_{Naphtha-lene}$	$m_{2,4-Xylenol}$	$m_{3,5-Xylenol}$	$m_{3,4-Xylenol}$	m_{TEG}	$m_{Solvent\ Phase}$	$m_{Hexane\ Phase}$	
x9a	75.000	1.063	1.015	4.020	6.020	2.023	1.010	1.029	7.544	12.157	85.826	-0.8
x9b	75.000	1.749	1.004	4.016	6.044	2.009	1.012	1.029	15.073	20.068	84.965	-1.8
x9c	75.000	2.548	1.014	4.021	6.010	2.055	1.023	1.021	23.146	30.395	85.025	-0.4
x9d	75.400	3.341	1.003	4.027	6.014	2.046	1.022	1.019	30.460	38.851	84.865	-0.5
x9e	75.200	5.026	1.010	4.064	6.039	2.020	1.016	1.014	45.047	55.155	84.851	-0.3
x10a	60.100	1.547	1.029	4.327	6.098	2.098	1.059	1.015	7.613	13.144	70.831	-1.1
x10b	60.800	1.691	1.032	4.034	6.136	2.024	1.003	1.002	15.242	21.343	70.081	-1.7
x10c	60.300	2.517	1.041	4.340	6.117	2.029	1.008	1.020	23.110	30.705	70.194	-0.6
x10d	60.200	3.369	1.010	4.088	6.123	2.018	1.049	1.049	31.577	39.815	69.619	-0.9
x10e	60.100	5.053	1.112	4.117	6.158	2.019	1.031	1.041	45.236	55.256	69.546	-0.8
x11a	45.500	0.849	1.008	4.034	6.077	2.028	1.010	1.012	7.527	12.471	54.567	-2.9
x11c	45.400	2.535	1.013	4.033	6.175	2.016	1.011	1.006	22.922	29.409	54.539	-2.5
x11d	45.400	3.330	1.032	4.055	6.135	2.026	1.030	1.002	30.089	38.325	53.293	-2.6
x11e	45.300	5.031	1.004	4.085	6.019	2.063	1.031	1.007	45.027	55.365	52.973	-2.0
x12a	60.200	0.920	1.001	4.011	6.068	2.059	1.026	1.014	7.611	12.549	70.827	-0.6
x12b	60.400	15.001	1.009	4.006	6.003	2.046	1.009	1.018	15.031	32.441	71.974	-1.1
x12c	62.200	22.554	1.014	4.059	6.004	2.114	1.009	1.007	22.572	45.945	74.055	-2.1
x12d	62.400	30.263	1.145	4.065	6.003	2.033	1.038	1.021	30.246	63.277	73.295	-1.2
x12e	62.100	45.090	1.032	4.043	6.009	2.008	1.016	1.032	45.314	93.399	72.194	-1.2
x13a	30.400	2.512	1.020	4.039	5.997	2.070	1.024	1.006	7.575	13.986	39.314	-0.4
x13b	30.400	5.026	1.022	4.018	6.010	2.105	1.007	1.019	15.455	24.884	40.418	-1.2
x13c	30.800	7.612	1.007	4.006	6.116	2.027	1.022	1.051	22.949	33.227	40.702	-3.5
x13d	31.600	10.135	1.029	4.028	6.036	2.022	1.027	1.035	30.309	44.612	39.208	-3.9
x13e	30.100	15.307	1.020	4.007	6.092	2.019	1.039	1.050	46.085	65.725	39.891	-1.0
x14a	30.600	0.835	1.006	4.135	6.036	2.017	1.006	1.037	7.506	13.584	40.137	-0.8
x14b	31.800	0.000	0.000	4.029	6.011	2.026	1.016	1.003	13.507	19.072	39.172	-1.9
x14c	45.200	0.000	0.000	4.110	6.028	2.024	1.003	1.033	22.768	28.829	52.553	-1.0
x14d	45.700	0.000	0.000	4.216	6.054	2.023	1.014	1.020	30.186	36.597	52.449	-1.3
x14e	31.400	0.000	0.000	4.663	6.056	2.020	1.005	1.040	46.531	53.738	37.321	-1.8
x15a	45.400	1.673	1.019	4.171	6.073	2.151	1.031	1.025	16.202	22.633	54.727	-1.8
x15b	31.600	1.683	1.019	4.457	6.072	2.045	1.014	1.023	15.923	22.429	41.234	-1.8
x15c	30.300	2.518	1.034	4.268	6.020	2.024	1.030	1.006	22.700	30.951	39.410	-0.8
x15d	31.400	3.348	1.015	4.167	6.024	2.181	1.005	1.021	30.500	39.761	39.345	-1.9
x15e	31.500	5.285	1.016	4.048	6.041	2.008	1.028	1.015	47.300	58.483	39.131	-1.6
x16a	30.700	5.636	1.075	4.027	6.033	2.022	1.038	1.037	8.066	17.081	39.678	-3.8
x16b	31.200	10.094	1.045	4.007	6.047	2.018	1.036	1.012	15.343	28.918	42.058	-1.2
x16c	31.700	15.094	1.136	4.120	6.121	2.080	1.010	1.029	22.900	41.568	42.590	-1.2
x16d	30.300	20.452	1.008	4.242	6.016	2.312	1.037	1.013	30.100	54.830	39.459	-2.3
x16e	30.900	30.808	1.022	4.024	6.092	2.004	1.036	1.023	45.200	79.599	41.329	-1.0

Table:A5.2. Mass of Hexane(1), Water(2), Indane(3), Dodecane(4), Naphthalene(5), 2,4-Xylenol(6), 3,5-Xylenol (7), 3,4-Xylenol (8) and Triethylene Glycol(9) in the Solvent and Antisolvent Phase for Batch Extractions using the Xylenol Feed Stream at 313.15K

Exp.	Masses of Components in Solvent Phase [g]									ε_{SP}	Masses of Components in Antisolvent Phase [g]									ε_{HP}	Mass Balance Errors over Components [%]								
ID	m_1^I	m_2^I	m_3^I	m_4^I	m_5^I	m_6^I	m_7^I	m_8^I	m_9^I	[%]	m_1^{II}	m_2^{II}	m_3^{II}	m_4^{II}	m_5^{II}	m_6^{II}	m_7^{II}	m_8^{II}	m_9^{II}	[%]	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8	ε_9
X1a	0.171	4.907	0.046	0.016	0.539	1.532	0.842	0.852	7.669	2.7	14.704	0.024	0.982	3.974	5.397	0.504	0.203	0.183	0.059	2.7	-2.2	-2.3	-1.3	-0.7	-1.3	0.0	-0.7	0.9	2.2
x1b	0.334	20.055	0.074	0.065	0.907	3.240	1.738	1.753	29.920	2.2	31.075	0.045	1.950	7.916	11.258	0.780	0.302	0.249	0.175	2.8	3.3	0.1	-1.1	-0.6	0.9	0.1	1.6	-2.5	0.2
x1c	0.241	15.129	0.033	0.028	0.439	1.724	0.920	0.926	22.157	0.4	15.027	0.023	1.060	4.104	5.635	0.310	0.099	0.105	0.022	1.8	-0.7	0.8	-0.6	2.2	0.0	0.8	0.9	-0.7	-2.3
x1d	0.095	20.018	0.029	0.003	0.440	1.794	0.929	0.924	30.135	1.0	15.848	0.008	1.014	3.955	5.508	0.291	0.098	0.078	0.093	3.0	0.9	-0.2	-2.6	-1.7	-0.9	1.2	-0.5	-0.6	0.6
x1e	0.096	29.938	0.015	0.005	0.504	1.852	0.946	0.929	47.183	3.2	15.003	0.006	0.995	3.915	5.524	0.227	0.073	0.061	0.095	0.4	-1.3	-1.5	-1.4	-3.3	-0.2	1.2	-1.1	-1.6	3.0
x2a	0.073	5.052	0.008	0.003	0.123	1.091	0.674	0.677	7.392	1.1	76.021	0.026	1.002	4.087	5.991	0.964	0.376	0.352	0.127	3.6	1.3	1.2	-0.3	2.0	0.4	2.5	1.7	2.5	0.0
x2b	0.076	10.024	0.014	0.040	0.142	1.303	0.749	0.775	14.997	0.7	75.390	0.019	1.012	3.984	6.045	0.735	0.266	0.245	0.163	1.4	0.4	-0.1	0.9	0.2	2.0	0.7	0.5	1.3	-0.3
x2c	0.093	15.133	0.003	0.006	0.125	1.447	0.827	0.821	22.433	0.9	75.960	0.017	1.042	3.930	6.000	0.634	0.220	0.183	0.034	1.5	0.9	0.0	-0.2	-2.1	1.4	2.8	1.4	0.4	-0.4
x2d	0.181	20.446	0.010	0.004	0.132	1.520	0.879	0.888	30.726	3.1	75.997	0.018	1.024	4.078	5.933	0.542	0.183	0.147	0.059	3.5	1.6	1.1	1.0	0.9	0.6	1.4	2.3	1.5	2.4
x2e	0.188	29.998	0.010	0.009	0.186	1.629	0.878	0.880	45.587	1.2	73.718	0.011	1.014	4.166	5.860	0.421	0.140	0.131	0.151	0.1	-2.1	-0.2	-0.3	0.9	0.3	1.2	-0.1	0.7	0.8
x3a	0.109	5.003	0.017	0.004	0.235	1.309	0.732	0.759	7.403	0.3	44.533	0.021	0.995	4.035	5.759	0.745	0.294	0.270	0.197	3.5	-1.7	0.2	-0.5	0.5	-0.8	2.6	2.2	2.6	1.3
x3b	0.103	9.921	0.012	0.001	0.208	1.489	0.755	0.871	15.080	0.7	44.228	0.013	1.026	4.072	5.841	0.551	0.259	0.192	0.173	0.3	-1.9	-1.1	1.6	1.3	0.6	1.8	-0.3	0.9	1.3
x3c	0.052	14.589	0.009	0.008	0.217	1.548	0.845	0.872	22.308	1.8	45.308	0.013	1.029	3.996	5.860	0.449	0.152	0.128	0.032	1.8	0.8	-3.3	1.1	0.0	-0.1	-0.2	-1.7	-1.9	-1.7
x3d	0.153	20.281	0.015	0.012	0.239	1.739	0.884	0.904	29.978	0.6	44.247	0.008	0.993	4.056	5.786	0.424	0.132	0.113	0.108	0.3	-1.6	0.0	-1.1	0.8	0.4	0.7	0.3	0.8	-0.2
x3e	0.109	29.652	0.012	0.009	0.305	1.754	0.911	0.916	45.462	0.9	45.332	0.007	1.019	4.019	5.614	0.321	0.099	0.108	0.422	2.5	-0.3	-1.2	1.0	0.3	-1.7	1.5	0.8	1.2	1.7
x4a	0.107	7.568	0.007	0.002	0.110	0.997	0.594	0.662	7.455	1.9	57.656	0.034	0.991	4.084	6.074	1.059	0.433	0.403	0.197	1.3	1.5	0.5	-0.3	1.8	1.5	1.6	2.4	1.8	1.8
x4b	0.226	13.413	0.001	0.006	0.217	1.924	1.084	1.160	19.526	0.4	80.550	0.023	1.315	5.304	7.624	0.795	0.280	0.252	0.196	1.3	0.6	0.2	0.9	1.2	-0.3	0.4	0.7	0.8	-1.5
x4c	0.130	14.785	0.002	0.009	0.183	1.534	0.839	0.869	22.440	0.0	59.469	0.011	1.025	4.171	5.942	0.523	0.173	0.148	0.081	2.3	-1.0	-1.6	1.4	-1.2	1.8	1.2	-0.9	-0.2	-0.2
x4d	0.279	20.217	0.010	0.002	0.197	1.634	0.889	0.889	30.718	1.8	56.280	0.010	1.005	4.048	5.943	0.455	0.145	0.124	0.078	1.8	2.3	0.0	0.2	0.2	1.9	3.0	2.3	1.3	2.2
x4e	0.311	27.561	0.014	0.006	0.215	1.618	0.894	0.890	45.043	2.1	59.571	0.007	1.031	4.223	5.895	0.390	0.139	0.119	0.056	-0.7	-1.0	0.9	1.8	-0.6	0.8	-1.9	-1.3	0.2	-0.4
x5a	0.125	4.846	0.012	0.003	0.183	1.298	0.759	0.787	7.246	-0.5	59.855	0.022	1.050	4.027	5.878	0.784	0.305	0.258	0.054	3.4	-1.0	-1.7	2.0	0.1	1.1	1.4	1.7	2.7	-2.8
x5b	0.138	4.961	0.018	0.002	0.335	1.652	0.903	0.873	15.205	1.5	61.739	0.009	1.070	4.011	5.823	0.378	0.123	0.158	0.203	1.4	1.6	-0.9	2.3	-0.1	1.2	0.2	0.5	1.4	1.7
x5c	0.149	7.589	0.018	0.002	0.386	1.732	0.918	0.937	22.684	2.6	60.549	0.005	1.007	4.035	5.760	0.298	0.090	0.183	0.236	1.7	2.6	1.1	1.6	0.3	1.6	1.0	-0.8	0.4	1.5
x5d	0.208	9.927	0.012	0.003	0.467	1.814	0.963	0.977	29.897	0.9	57.001	0.007	1.003	4.018	5.679	0.249	0.083	0.069	0.050	1.3	2.3	-1.0	0.4	0.3	1.2	3.1	1.0	0.7	-0.2
x5e	0.190	15.198	0.030	0.003	0.488	1.835	0.941	0.973	44.938	1.3	58.581	0.005	0.989	4.041	5.695	0.187	0.061	0.055	0.072	0.7	2.3	0.9	0.3	-1.0	1.3	0.7	-0.2	1.4	-0.4
x6a	0.275	5.285	0.022	0.010	0.358	1.636	0.872	0.918	14.969	-0.3	45.432	0.016	0.990	4.087	5.596	0.360	0.098	0.104	0.180	2.7	0.2	-0.1	-0.1	0.2	-1.5	-0.9	-3.3	-1.6	-2.8

Table:A5.2. Mass of Hexane(1), Water(2), Indane(3), Dodecane(4), Naphthalene(5), 2,4-Xylenol(6), 3,5-Xylenol (7), 3,4-Xylenol (8) and Triethylene Glycol(9) in the Solvent and Antisolvent Phase for Batch Extractions using the Xylenol Feed Stream at 313.15K (cont.)

Exp.	Masses of Components in Solvent Phase [g]									ε_{SP}	Masses of Components in Antisolvent Phase [g]									ε_{HP}	Mass Balance Errors over Components [%]								
ID	m_1^I	m_2^I	m_3^I	m_4^I	m_5^I	m_6^I	m_7^I	m_8^I	m_9^I	[%]	m_1^{II}	m_2^{II}	m_3^{II}	m_4^{II}	m_5^{II}	m_6^{II}	m_7^{II}	m_8^{II}	m_9^{II}	[%]	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8	ε_9
x6b	0.166	2.512	0.029	0.003	0.404	1.606	0.877	0.924	7.565	-1.8	43.593	0.016	1.012	4.056	5.668	0.456	0.145	0.142	0.105	3.3	-2.8	0.0	1.6	0.9	0.6	1.8	1.3	2.5	-1.1
x6c	0.188	7.304	0.026	0.011	0.476	1.777	0.936	0.979	22.474	1.0	43.739	0.008	1.004	4.047	5.421	0.251	0.089	0.075	0.101	-1.5	-0.6	-3.0	0.5	0.8	-1.9	0.0	0.4	1.2	0.3
x6d	0.196	11.069	0.030	0.002	0.627	1.837	1.107	1.039	32.571	0.3	48.744	0.008	1.101	4.413	6.059	0.218	0.077	0.078	0.152	2.9	1.6	0.2	0.5	0.0	-0.4	2.1	-0.7	1.3	-1.3
x6e	0.204	15.468	0.042	0.004	0.627	1.908	1.005	1.018	45.343	1.9	43.171	0.011	0.998	4.063	5.416	0.198	0.065	0.065	0.173	0.6	2.0	3.0	2.3	0.4	0.0	3.4	3.7	3.4	0.2
x7a	0.156	2.636	0.020	0.013	0.232	1.404	0.787	0.834	7.467	1.5	74.712	0.014	0.994	4.014	5.785	0.666	0.243	0.210	0.086	2.7	-1.1	2.9	0.6	-0.2	-0.3	2.2	1.7	2.6	-0.9
x7b	0.215	5.099	0.028	0.004	0.488	1.777	0.977	0.971	24.801	0.8	74.524	0.007	1.002	4.040	5.618	0.291	0.104	0.089	0.142	0.2	-1.1	1.8	1.1	0.3	-0.6	2.2	2.3	0.4	-0.7
x7c	0.170	7.729	0.019	0.005	0.310	1.688	0.908	0.915	22.980	1.5	74.573	0.012	1.004	4.081	5.850	0.381	0.129	0.107	0.244	1.6	1.3	0.6	2.0	1.3	1.1	2.6	2.4	1.7	3.0
x7d	0.248	30.253	0.016	0.015	0.220	1.704	0.903	0.928	45.882	1.9	59.107	0.009	1.014	4.197	5.833	0.373	0.117	0.103	0.161	0.4	1.4	0.8	1.9	2.1	0.3	2.3	1.5	1.4	1.1
x7e	0.195	15.230	0.026	0.007	0.456	1.821	0.927	0.941	45.005	0.3	75.039	0.013	1.029	4.095	5.783	0.217	0.072	0.076	0.451	2.9	2.8	1.6	2.0	0.5	1.6	1.6	-2.2	-0.8	0.4
x8a	0.134	2.519	0.019	0.003	0.304	1.488	0.820	0.852	7.317	0.2	59.787	0.015	1.000	4.057	5.728	0.569	0.201	0.182	0.309	2.6	-0.5	-0.2	0.9	0.5	-1.7	1.2	0.7	2.0	0.4
x8b	0.260	5.147	0.015	0.009	0.274	1.578	0.892	0.871	14.726	1.5	74.537	0.011	0.995	4.064	5.776	0.500	0.174	0.161	0.267	0.3	-1.1	0.7	-0.7	1.6	0.3	2.8	0.4	0.4	-0.6
x8c	0.352	11.248	0.079	0.017	1.471	2.858	1.486	1.518	34.294	1.3	22.234	0.006	1.406	6.015	7.679	0.228	0.075	0.068	0.139	2.5	-0.5	-0.3	-1.1	0.4	1.2	1.9	1.6	1.8	0.8
x8d	0.300	11.158	0.033	0.044	0.403	1.951	1.037	1.057	33.630	1.2	83.544	0.010	1.139	4.455	6.458	0.321	0.100	0.098	0.119	0.2	1.2	-2.2	2.5	0.1	1.5	0.5	-0.3	2.2	-0.3
x8e	0.328	22.222	0.105	0.002	1.842	2.967	1.497	1.501	66.023	-0.7	22.327	0.004	1.420	6.110	7.126	0.147	0.044	0.040	0.119	0.3	-0.2	-1.7	0.4	0.2	-2.2	1.3	0.8	1.9	-2.0
x9a	0.238	1.083	0.022	0.011	0.354	1.420	0.787	0.825	7.590	1.4	74.533	0.013	1.000	4.036	5.760	0.590	0.213	0.188	0.076	0.7	-0.3	3.1	0.7	0.7	1.6	-0.7	-1.0	-1.5	1.6
x9b	0.314	1.793	0.037	0.010	0.502	1.643	0.883	0.910	14.847	3.3	74.683	0.008	0.990	4.068	5.493	0.349	0.138	0.116	0.341	1.4	0.0	3.0	2.3	1.6	-0.8	-0.9	1.0	-0.3	0.8
x9c	0.345	2.635	0.067	0.012	0.679	1.872	0.962	0.969	23.167	1.0	75.440	0.007	0.962	3.923	5.371	0.228	0.085	0.090	0.078	1.4	1.0	3.7	1.5	-2.1	0.7	2.2	2.3	3.5	0.4
x9d	0.394	3.418	0.068	0.016	0.779	1.812	0.945	0.969	30.897	1.2	74.819	0.005	0.960	4.066	5.248	0.217	0.074	0.064	0.303	1.1	0.6	2.5	2.6	1.4	0.2	-0.8	-0.3	1.4	2.4
x9e	0.496	5.137	0.086	0.019	0.998	1.922	0.992	0.951	44.938	0.7	74.885	0.005	0.948	4.009	5.072	0.108	0.028	0.054	0.145	0.5	0.2	2.3	2.3	-0.9	0.5	0.5	0.4	-0.9	0.1
x10a	0.231	1.545	0.027	0.003	0.401	1.666	0.888	0.871	7.519	0.1	60.062	0.011	1.007	4.333	5.609	0.424	0.182	0.161	0.132	1.5	0.3	0.6	0.5	0.2	-1.4	-0.4	1.0	1.7	0.5
x10b	0.362	1.714	0.033	0.015	0.564	1.691	0.896	0.917	15.083	-0.3	60.066	0.010	1.002	3.924	5.429	0.359	0.118	0.106	0.079	1.4	-0.6	2.0	0.3	-2.4	-2.3	1.3	1.1	2.1	-0.5
x10c	0.361	2.613	0.050	0.008	0.800	1.809	0.947	0.972	23.035	-0.4	61.202	0.013	0.999	4.334	5.370	0.208	0.077	0.056	0.065	3.0	2.1	-3.8	0.8	0.0	0.9	-0.6	1.6	0.8	0.0
x10d	0.495	3.349	0.055	0.012	0.963	1.906	1.004	1.012	30.981	-0.1	60.287	0.007	0.973	4.075	5.151	0.178	0.067	0.058	0.230	2.0	2.8	-0.4	1.8	0.0	-0.1	3.3	2.1	2.0	-1.2
x10e	0.573	5.081	0.072	0.041	1.239	1.878	0.997	0.994	45.349	1.8	60.406	0.004	1.060	4.238	5.025	0.119	0.036	0.041	0.116	2.2	1.5	0.6	1.8	3.9	1.7	-1.1	0.2	-0.6	0.5
x11a	0.393	0.845	0.042	0.017	0.649	1.595	0.862	0.860	7.527	2.6	44.960	0.008	0.983	4.104	5.511	0.458	0.149	0.150	0.160	3.5	-0.3	0.4	1.7	2.1	1.4	1.2	0.1	-0.2	2.1
x11c	0.489	2.463	0.057	0.029	1.045	1.862	0.951	0.954	22.560	3.4	45.528	0.005	0.967	3.943	5.277	0.152	0.046	0.050	0.366	3.3	1.4	-2.6	1.1	-1.5	2.4	-0.1	-1.4	-0.2	0.0
x11d	0.435	3.333	0.074	0.013	1.149	1.921	1.002	0.998	30.751	3.5	43.588	0.003	0.948	4.060	5.162	0.164	0.058	0.049	0.077	1.5	-3.0	0.2	-1.0	0.4	2.9	2.9	2.8	0.4	2.5
x11e	0.543	5.049	0.082	0.006	1.429	1.988	1.004	0.995	44.867	1.1	42.896	0.004	0.927	4.117	4.794	0.082	0.026	0.024	0.100	0.0	0.9	0.4	0.6	0.9	3.4	0.3	-0.1	1.3	-0.1

Table:A5.2. Mass of Hexane(1), Water(2), Indane(3), Dodecane(4), Naphthalene(5), 2,4-Xylenol(6), 3,5-Xylenol (7), 3,4-Xylenol (8) and Triethylene Glycol(9) in the Solvent and Antisolvent Phase for Batch Extractions using the Xylenol Feed Stream at 313.15K (cont.)

Exp.	Masses of Components in Solvent Phase [g]									ε_{SP}	Masses of Components in Antisolvent Phase [g]									ε_{HP}	Mass Balance Errors over Components [%]								
ID	m_1^I	m_2^I	m_3^I	m_4^I	m_5^I	m_6^I	m_7^I	m_8^I	m_9^I	[%]	m_1^{II}	m_2^{II}	m_3^{II}	m_4^{II}	m_5^{II}	m_6^{II}	m_7^{II}	m_8^{II}	m_9^{II}	[%]	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8	ε_9
x12a	0.355	0.945	0.032	0.006	0.470	1.630	0.876	0.885	7.590	1.9	58.400	0.015	0.987	4.039	5.483	0.423	0.154	0.132	0.124	-1.5	-2.4	-3.9	1.8	0.9	-1.9	-0.3	0.4	0.2	1.4
x12b	0.146	14.651	0.007	0.008	0.104	1.155	0.670	0.713	15.048	0.2	60.043	0.026	1.004	3.999	5.979	0.931	0.354	0.306	0.066	1.0	-0.3	-2.2	0.2	0.0	1.3	1.9	1.5	0.2	0.6
x12c	0.163	21.891	0.006	0.010	0.095	1.250	0.681	0.703	21.687	1.2	61.461	0.027	1.008	4.051	5.942	0.872	0.330	0.283	0.076	0.0	-0.9	-2.8	0.0	0.0	0.6	0.4	0.2	-2.1	-3.6
x12d	0.141	29.693	0.027	0.051	0.112	1.357	0.786	0.795	30.598	0.4	60.465	0.022	1.103	4.031	5.942	0.686	0.247	0.203	0.091	-0.7	-2.9	-1.8	-1.3	0.4	0.9	0.5	-0.5	-2.3	1.5
x12e	0.525	43.667	0.009	0.005	0.125	1.485	0.828	0.858	45.514	-0.4	62.265	0.022	1.019	4.109	5.902	0.546	0.175	0.156	0.074	2.9	1.1	-3.1	-0.4	1.7	0.3	1.1	-1.2	-1.7	0.6
x13a	0.273	2.398	0.039	0.008	0.549	1.659	0.865	0.863	7.561	1.6	28.993	0.012	0.981	3.994	5.272	0.378	0.133	0.122	0.029	1.5	-3.7	-3.7	0.0	-0.9	-2.9	-1.6	-2.5	-2.0	0.2
x13b	0.219	4.896	0.036	0.005	0.591	1.865	0.925	0.943	14.899	-2.0	30.823	0.008	1.001	4.057	5.423	0.256	0.082	0.075	0.079	3.4	2.1	-2.4	1.5	1.1	0.1	0.8	0.0	-0.1	-3.1
x13c	0.235	7.406	0.035	0.010	0.635	1.769	0.911	0.946	22.278	3.0	30.940	0.007	1.009	4.093	5.596	0.200	0.071	0.066	0.329	4.0	1.2	-2.6	3.2	2.4	1.9	-2.9	-3.2	-3.7	-1.5
x13d	0.288	9.813	0.036	0.008	0.786	1.878	0.960	0.991	30.922	2.4	28.102	0.010	1.000	4.166	5.330	0.181	0.056	0.045	0.070	-0.6	0.7	-3.1	0.6	3.6	1.3	1.9	-1.1	0.1	2.3
x13e	0.489	15.048	0.047	0.046	0.908	1.912	0.996	1.017	47.052	2.7	29.982	0.009	0.963	3.898	5.164	0.115	0.038	0.034	0.088	1.0	1.2	-1.6	-1.1	-1.6	-0.3	0.4	-0.5	0.1	2.3
x14a	0.460	0.851	0.067	0.018	0.960	1.755	0.920	0.942	7.406	-1.5	30.130	0.009	0.964	4.043	5.246	0.306	0.112	0.102	0.099	2.2	0.0	3.0	2.5	-1.8	2.8	2.2	2.6	0.7	0.0
x14b	0.624	0.000	0.000	0.029	1.449	1.868	0.953	0.936	13.632	2.2	31.242	0.000	0.000	4.003	4.465	0.157	0.055	0.049	0.063	2.2	0.2	0.0	0.0	0.1	-1.6	-0.1	-0.7	-1.8	1.4
x14c	0.754	0.000	0.000	0.031	1.664	1.968	0.987	0.998	21.924	-1.7	45.681	0.000	0.000	4.185	4.464	0.119	0.039	0.037	0.058	3.9	2.7	0.0	0.0	2.6	1.7	3.1	2.3	0.2	-3.5
x14d	0.694	0.000	0.000	0.031	1.959	1.934	0.972	1.014	30.339	0.9	44.507	0.000	0.000	4.108	4.233	0.078	0.027	0.018	0.126	1.2	-1.1	0.0	0.0	-1.8	2.3	-0.6	-1.6	1.2	0.9
x14e	1.176	0.000	0.000	0.069	2.869	1.982	0.984	0.995	45.536	-0.2	30.217	0.000	0.000	4.549	3.241	0.039	0.013	0.012	0.049	2.1	0.0	0.0	0.0	-1.0	0.9	0.0	-0.8	-3.2	-2.0
x15a	0.265	1.670	0.061	0.006	1.031	1.933	0.991	0.981	16.777	0.5	46.383	0.004	0.936	4.089	4.908	0.179	0.054	0.046	0.057	3.5	2.7	0.1	-2.2	-1.8	-2.2	-1.8	1.4	0.2	3.9
x15b	0.347	1.664	0.058	0.013	1.213	1.894	0.951	0.954	15.730	1.8	31.195	0.004	1.022	4.277	4.946	0.147	0.048	0.044	0.061	1.2	-0.2	-0.9	0.0	-3.7	1.4	-0.2	-1.5	-2.5	-0.8
x15c	0.336	2.578	0.075	0.012	1.517	1.946	0.981	0.931	22.900	1.0	29.727	0.005	1.008	4.172	4.432	0.106	0.036	0.041	0.060	0.5	-0.8	2.6	2.8	-2.0	-1.2	1.4	-1.3	-3.4	1.1
x15d	0.575	3.443	0.087	0.016	1.765	2.154	0.993	0.976	29.483	-0.7	30.723	0.006	0.892	4.033	4.262	0.084	0.023	0.028	0.109	2.1	-0.3	3.0	-3.5	-2.8	0.1	2.6	1.1	-1.7	-3.0
x15e	0.515	5.375	0.109	0.008	1.908	1.959	1.020	0.988	47.376	1.3	30.849	0.006	0.939	4.154	4.020	0.059	0.016	0.017	0.072	2.6	-0.4	1.8	3.2	2.8	-1.9	0.5	0.8	-1.0	0.3
x16a	0.128	5.555	0.025	0.006	0.301	1.438	0.838	0.858	7.874	-0.3	28.989	0.020	1.048	3.952	5.678	0.602	0.229	0.196	0.361	3.5	2.6	-1.1	-0.1	-1.7	-0.9	0.9	2.8	1.6	2.1
x16b	0.120	10.011	0.017	0.002	0.272	1.553	0.885	0.879	15.158	-0.1	30.294	0.013	1.006	3.958	5.683	0.527	0.161	0.138	0.052	-0.5	-2.5	-0.7	-2.1	-1.2	-1.5	3.1	1.0	0.5	-0.9
x16c	0.125	14.798	0.017	0.002	0.287	1.693	0.895	0.916	22.397	-1.1	30.920	0.011	1.110	4.029	5.876	0.394	0.123	0.108	0.064	0.1	-2.1	-1.9	-0.8	-2.1	0.7	0.4	0.7	-0.5	-1.9
x16d	0.289	20.029	0.090	0.002	0.308	1.886	0.898	0.916	29.674	-1.3	29.574	0.009	0.942	4.156	5.595	0.424	0.172	0.119	0.083	4.0	-1.4	-2.0	2.4	-2.0	-1.9	-0.1	3.1	2.2	-1.1
x16e	0.657	30.534	0.114	0.003	0.358	1.669	0.922	0.927	45.078	0.8	28.021	0.008	0.925	4.042	7.889	0.363	0.135	0.074	0.123	0.6	-3.5	-0.9	1.7	0.5	0.0	1.4	2.0	-2.1	0.0

A6. Batch Extractions for Generation of LLE data for m-p-Cresol System

Table A6-1. Masses of Components Added to Separating Funnel at 313.15K.

	Masses of Components into the Separating Funnels [g]						Masses of Resulting Phases [g]		$\varepsilon_{In/Out}$
No.	m_{hexane}	m_{water}	$m_{o\text{-}tolunitrile}$	$m_{m\text{-}Cresol}$	$m_{p\text{-}Cresol}$	m_{TEG}	$m_{Solvent\ Phase}$	$m_{Hexane\ Phase}$	[%]
1c	29.979	2.014	1.015	2.523	2.509	18.03	25.487	28.773	-3.2
2c	36.218	4.571	1.289	3.047	3.100	15.064	25.93	36.033	-2.1
2d	35.986	8.913	1.247	3.048	3.115	14.68	29.738	35.052	-3.3
4a	25.550	7.723	1.064	2.601	2.603	25.076	37.952	24.133	-3.9
5b	25.033	7.370	1.382	3.386	3.400	24.49	39.333	23.842	-2.9
7a	28.696	6.586	1.211	2.992	2.994	21.583	33.972	27.424	-4.2
7b	14.426	6.475	1.229	2.993	2.991	21.605	34.664	12.881	-4.4
7c	7.327	6.403	1.200	2.993	2.990	21.482	34.595	6.435	-3.2
7d	21.699	2.167	1.192	3.019	3.003	21.592	30.602	20.434	-3.1
8a	22.273	4.501	1.236	3.026	3.030	21.87	32.944	21.694	-2.3
8b	21.669	8.655	1.196	3.010	3.003	21.639	36.563	21.163	-2.4
9a	21.635	8.633	1.195	2.996	3.001	21.585	36.453	21.372	-2.1
9b	21.648	10.827	1.196	2.996	3.006	21.612	38.508	20.595	-3.6
10a	21.662	5.524	1.242	2.991	2.993	18.058	30.049	21.145	-2.4
10e	36.090	1.076	1.191	3.000	3.019	10.849	18.441	35.183	-2.9
11a	21.796	4.371	1.237	3.014	3.006	14.517	25.377	20.628	-4.0
11b	21.836	3.297	1.225	3.004	2.998	10.957	20.755	20.764	-4.2
12b	36.023	2.263	1.192	3.010	2.992	10.797	19.269	35.886	-2.0
12d	36.202	5.520	1.245	2.998	2.996	10.859	22.385	36.147	-2.2
13b	36.577	8.848	1.232	2.996	3.076	21.968	36.806	36.076	-2.4
13c	36.108	10.93	1.21	3.013	3.011	21.673	38.730	34.198	-4.0
13d	36.576	5.541	1.258	2.999	3.053	18.343	30.101	34.855	-4.2
14a	36.418	10.81	1.207	3.010	2.993	36.067	52.914	35.901	-1.9
14b	36.012	4.368	1.201	2.998	3.000	10.863	21.156	35.549	-3.0
14c	36.931	3.258	1.207	3.004	3.000	10.817	20.143	36.460	-2.8

Table:A6.2. Mass of Hexane(1), Water(2o-Tolunitrile(3),p-Cresol(4), m-Cresol(5), and Triethylene Glycol(6) in the Solvent and Antisolvent Phase for Batch Extractions for Generation of LLE Data for m,-p-Cresol System at 313.15K

	Masses of components in Solvent Phase [g]						ε_{SP}	Masses of components in Antisolvent Phase [g]							ε_{HP}	Errors on Mass Balance					
No.	m^{I}_{hexane}	m^{I}_{water}	$m^{I}_{o\text{-}tolunitrile}$	$m^{I}_{p\text{-}cresol}$	$m^{I}_{m\text{-}cresol}$	m^{I}_{TEG}	[%]	m^{II}_{hexane}	m^{II}_{water}	$m^{II}_{o\text{-}tolunitrile}$	$m^{II}_{p\text{-}cresol}$	$m^{II}_{m\text{-}cresol}$	m^{II}_{TEG}	m^{II}_{hexane}	[%]	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6
1c	0.438	2.039	0.522	2.320	2.364	18.499	2.7	27.598	0.007	0.459	0.104	0.082	4.526	0.000	-1.8	1.6	-1.1	-3.4	-3.4	-3.0	2.6
2c	0.515	4.641	0.600	3.035	2.976	15.618	5.6	34.507	0.004	0.653	0.143	0.119	9.286	0.000	-1.7	1.6	1.3	-2.8	2.5	1.6	3.7
2d	0.455	8.847	0.492	3.011	2.974	14.049	0.3	33.863	0.004	0.766	0.163	0.158	5.007	0.000	-0.3	-0.7	0.1	0.9	1.9	2.7	-4.3
4a	0.307	7.666	0.554	2.591	2.478	25.827	3.9	23.208	0.002	0.516	0.052	0.040	4.304	0.014	-1.2	-0.7	0.3	0.6	1.6	-3.2	3.1
5b	0.532	7.631	0.787	3.279	3.234	24.525	1.7	22.972	0.005	0.538	0.074	0.063	5.446	0.018	-0.7	3.6	-0.9	-4.1	-1.4	-2.6	0.2
7a	0.397	6.659	0.619	2.902	2.852	22.013	4.3	25.627	0.004	0.565	0.079	0.070	4.045	0.007	-3.9	1.2	-0.4	-2.3	-0.4	-2.3	2.0
7b	0.527	6.621	0.849	2.883	2.875	21.702	2.3	11.867	0.003	0.372	0.036	0.032	2.057	0.004	-4.4	2.3	-0.6	-0.7	-2.4	-2.9	0.5
7c	0.591	6.608	0.972	2.913	2.933	21.267	2.0	6.279	0.001	0.211	0.019	0.016	0.989	0.004	1.5	3.2	-0.5	-1.4	-1.9	-1.5	-1.0
7d	0.404	2.234	0.829	2.942	2.917	21.279	0.0	20.397	0.002	0.359	0.042	0.034	2.929	0.000	2.0	3.2	-0.3	-0.3	-0.6	-2.3	-1.4
8a	0.603	4.645	0.717	2.935	2.928	21.825	2.2	20.902	0.002	0.497	0.058	0.052	3.088	0.000	-0.8	3.2	-0.3	-1.8	-1.2	-1.5	-0.2
8b	0.445	8.702	0.645	2.868	2.890	22.328	3.6	20.856	0.003	0.537	0.066	0.056	3.048	0.000	1.7	0.6	-0.4	-1.2	-2.3	-2.1	3.2
9a	0.490	8.767	0.679	2.931	2.921	21.712	2.9	20.089	0.002	0.541	0.070	0.060	3.282	0.000	-2.9	1.6	0.7	2.1	0.0	-0.5	0.6
9b	0.331	10.821	0.672	2.904	2.953	20.870	0.1	20.468	0.003	0.483	0.080	0.069	3.379	0.000	2.5	0.0	-1.4	-3.5	-0.7	0.9	-3.4
10a	1.739	5.619	0.723	2.859	2.863	17.925	5.6	19.688	0.002	0.543	0.067	0.058	3.246	0.002	-3.7	1.8	-0.3	1.9	-2.3	-2.3	-0.7
10e	1.180	1.094	0.637	2.892	2.866	10.410	3.5	33.651	0.003	0.582	0.190	0.175	5.379	0.180	-1.1	2.0	1.1	2.4	2.1	1.4	-2.4
11a	0.358	4.581	0.736	2.908	2.925	14.336	1.8	20.520	0.004	0.550	0.077	0.072	2.702	0.005	2.9	4.9	1.3	3.9	-0.7	-0.6	-1.2
11b	0.180	3.259	0.655	2.921	2.934	10.992	0.9	20.190	0.004	0.592	0.102	0.093	4.175	0.000	1.0	-1.1	0.5	1.8	0.8	0.8	0.3
12b	0.803	2.370	0.563	2.748	2.753	10.781	3.9	35.535	0.004	0.652	0.144	0.128	5.834	0.008	1.6	4.9	-0.2	2.0	-3.4	-4.3	-0.1
12d	0.495	5.630	0.474	2.792	2.794	11.208	4.5	34.407	0.007	0.789	0.196	0.184	7.280	0.005	-1.5	2.1	1.2	1.4	-0.3	-0.6	3.3
13b	0.473	8.686	0.541	2.967	2.885	21.946	1.9	35.219	0.009	0.718	0.106	0.088	5.090	0.004	0.2	-1.7	-0.1	2.2	-0.1	-0.8	-0.1
13c	0.178	10.980	0.497	2.890	2.891	22.125	2.1	35.635	0.005	0.732	0.115	0.107	5.012	0.003	7.0	0.5	0.7	1.6	-0.2	-0.5	2.1
13d	0.445	5.539	0.625	2.885	2.835	18.523	2.5	33.333	0.000	0.678	0.093	0.079	4.743	0.002	-1.9	0.0	-0.2	3.5	-2.5	-2.8	1.0
14a	0.250	10.609	0.663	2.824	2.841	35.503	-0.4	35.678	0.004	0.561	0.096	0.085	5.937	0.025	1.5	-1.8	-1.4	1.4	-2.5	-2.8	-1.5
14b	0.173	4.252	0.516	2.912	2.855	10.887	2.1	35.628	0.009	0.681	0.157	0.149	4.037	0.002	3.0	-2.4	0.0	-0.3	2.3	0.2	0.2
14c	0.621	3.233	0.530	2.812	2.809	10.517	1.9	36.030	0.000	0.715	0.120	0.105	4.165	0.004	1.4	-0.8	-1.1	3.1	-2.3	-3.0	-2.7

A7. Batch Extractions for Generation of LLE data for Aniline-Cresol System

Table A7-1. Masses of Components Added to Separating Funnel at 313.15K.

No.	Masses of Components added to Separating Funnels [g]							Masses of Resulting Phases [g]		$\varepsilon_{In/Out}$
	m_{hexane}	m_{water}	$m_{aniline}$	$m_{o\text{-}tolnitirle}$	$m_{m\text{-}Cresol}$	$m_{p\text{-}Cresol}$	m_{TEG}	$m_{Solvent\ Phase}$	$m_{Hexane\ Phase}$	[%]
amp2	61.500	1.661	1.025	1.542	6.065	7.329	15.100	31.785	60.461	-2.1
amp3	61.500	2.547	1.198	1.734	6.359	5.913	22.500	39.286	59.614	-2.8
amp4	62.500	3.421	1.031	1.650	6.335	8.403	30.400	50.647	60.244	-2.5
amp5	61.500	4.911	1.101	1.568	6.902	5.423	45.100	64.130	60.370	-1.6
amp8	62.000	8.375	1.075	1.027	5.533	10.073	22.900	48.131	59.863	-2.7
amp9	60.200	10.045	1.012	1.104	5.866	12.400	31.100	61.384	59.033	-1.1
amp10	61.200	15.549	1.086	1.062	5.443	8.065	45.800	75.900	57.200	-3.7
amp12	45.200	2.896	0.526	0.066	4.085	2.526	21.869	31.805	44.257	-1.4
amp13	35.200	1.452	0.476	0.100	3.687	2.299	19.951	27.900	35.290	0.0
amp14	36.700	2.679	0.445	0.056	3.829	2.375	19.863	29.420	36.034	-0.7
amp15	30.700	2.752	0.429	0.056	3.491	2.162	19.340	29.830	30.233	1.9

Table:A7.2. Mass of Hexane(1), Water(2), Aniline(3), o-Tolunitrile(4),m-Cresol(5), p-Cresol(6), and Triethylene Glycol(7) in the Solvent and Antisolvent Phase for Batch Extractions for Generation of LLE Data for m,-p-Cresol System at 313.15K

	Masses of Components in Solvent Phase [g]							ε_{SP}	Masses of Components in Antisolvent Phase [g]							ε_{HP}	Errors on Mass Balance [%]						
No.	m^{I}_{hexane}	m^{I}_{water}	$m^{I}_{aniline}$	$m^{I}_{o\text{-}tolunitrile}$	$m^{I}_{m\text{-}cresol}$	$m^{I}_{p\text{-}cresol}$	m^{I}_{TEG}	[%]	m^{II}_{hexane}	m^{II}_{water}	$m^{II}_{aniline}$	$m^{II}_{o\text{-}tolunitrile}$	$m^{II}_{m\text{-}cresol}$	$m^{II}_{p\text{-}cresol}$	m^{II}_{TEG}	[%]	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7
amp2	2.334	1.716	0.886	0.869	5.704	6.665	14.677	3.4	59.172	0.006	0.154	0.657	0.289	0.383	0.053	0.4	3.7	0.0	1.5	-1.0	-3.8	-1.2	-1.2
amp3	1.873	2.632	1.067	0.977	6.121	5.464	22.202	2.7	58.390	0.005	0.156	0.786	0.198	0.197	0.035	0.3	3.5	-2.0	2.1	1.7	-4.3	-0.6	-0.6
amp4	0.961	3.444	0.897	0.990	6.013	7.861	30.688	0.4	59.272	0.004	0.106	0.637	0.143	0.211	0.036	0.3	0.8	-3.6	-2.7	-1.4	-3.9	-2.8	-2.8
amp5	0.524	5.002	1.027	0.966	6.556	5.115	42.813	-3.3	58.971	0.004	0.084	0.609	0.106	0.096	0.990	0.8	1.9	-3.3	1.0	0.5	-3.9	-3.5	-3.5
amp8	2.319	8.279	0.942	0.583	5.307	9.502	23.090	3.9	56.692	0.010	0.133	0.445	0.170	0.338	0.262	-3.0	-1.0	-4.8	0.1	0.1	-2.3	-1.0	-1.0
amp9	2.499	10.190	0.937	0.690	5.757	11.980	32.084	4.5	56.330	0.005	0.095	0.417	0.128	0.276	0.014	-3.0	1.5	-2.3	1.9	0.3	-1.2	0.3	0.3
amp10	2.370	15.863	0.997	0.595	5.187	7.602	45.287	2.6	56.095	0.004	0.104	0.465	0.084	0.167	0.023	-0.5	2.0	-4.5	1.4	-0.2	-3.7	-3.1	-3.1
amp12	0.818	2.894	0.479	0.036	4.007	2.472	21.862	2.4	45.200	0.002	0.047	0.030	0.079	0.054	0.007	2.6	0.0	1.8	0.0	0.1	0.0	0.0	0.0
amp13	1.290	1.451	0.445	0.064	3.637	2.259	19.946	4.3	35.200	0.001	0.031	0.037	0.050	0.041	0.006	0.2	0.0	3.7	1.3	0.0	0.2	0.0	0.0
amp14	1.006	2.677	0.406	0.031	3.766	2.324	19.861	2.2	36.700	0.002	0.039	0.025	0.063	0.052	0.002	2.4	-0.1	2.7	0.0	0.0	0.1	-0.1	-0.1
amp15	0.875	2.750	0.396	0.033	3.435	2.116	19.331	-3.0	30.700	0.002	0.034	0.023	0.056	0.047	0.009	2.1	0.0	2.9	0.0	5.4	0.0	0.0	0.0

A8 Batch Extraction Data for TEG monomethyl ether

Table A8.1: Masses of Components Added to Separating Funnels at 313.15K

Exp. ID	Masses of Components In [g]								Masses of Resulting Phases [g]		ε_{MB}
	m_{hexane}	m_{water}	$m_{mesitylene}$	m_{EMP}	$m_{aniline}$	$m_{benzonitrile}$	m_{Phenol}	m_{TEG}	$m_{Solvent\ Phase}$	$m_{Hexane\ Phase}$	In/Out [%]
e1a	46.300	10.004	1.760	1.007	11.061	1.036	1.049	30.587	54.142	47.130	-1.5
e1b	46.100	20.465	1.403	1.010	10.673	1.006	1.006	30.348	63.114	47.848	-0.9
e1c	46.200	5.009	1.426	1.033	10.990	1.009	1.045	15.425	32.863	47.352	-2.3
e1d	75.000	10.067	1.375	1.011	10.909	1.174	1.120	30.255	53.129	75.246	-1.9
e1e	75.100	20.510	1.375	1.072	10.651	1.047	1.097	30.541	62.688	82.492	2.7
e2a	46.700	15.031	1.392	1.016	10.883	1.021	1.015	46.099	75.409	46.886	-0.7
e2b	46.400	30.422	1.395	1.032	10.911	1.016	1.018	45.053	87.791	48.068	-1.0
e2c	45.800	5.037	1.413	1.004	10.872	1.004	1.013	45.856	65.082	44.776	-1.9
e2d	46.700	30.145	1.394	1.007	10.823	1.037	1.243	22.818	64.721	47.514	-2.5
e2e	47.500	15.085	1.336	1.031	10.745	1.003	1.011	22.589	49.980	48.386	-1.9
e3a	22.600	1.695	0.668	0.502	5.557	0.518	0.505	7.759	16.379	22.613	-2.0
e3b	22.600	2.718	0.681	0.513	5.533	0.508	0.501	7.587	17.229	22.803	-1.5
e3c	22.500	5.313	0.695	0.515	5.407	0.528	0.514	7.606	18.834	23.458	-1.8
e3d	30.700	5.229	0.715	0.520	5.388	0.517	0.521	15.131	27.253	30.735	-1.2
e3e	30.900	3.322	0.681	0.510	5.352	0.501	0.540	10.312	19.997	31.030	-2.1
e4a	45.000	0.781	1.390	1.018	10.745	1.027	1.016	7.956	21.932	45.530	-2.1
e4b	47.000	2.563	1.446	1.021	10.629	1.002	1.029	7.754	22.580	49.020	-1.2
e4c	45.600	5.050	1.359	1.045	10.678	1.058	1.086	7.621	24.859	47.350	-1.8
e4d	30.600	2.567	1.366	1.059	10.714	1.019	1.059	7.850	24.477	29.813	-3.5
e4e	60.600	2.556	1.424	1.008	10.829	1.016	1.019	7.564	22.894	60.694	-2.8
e5a	75.100	2.560	1.558	1.044	10.786	1.016	1.006	8.590	23.457	75.529	-2.6
e5b	75.500	5.014	1.452	1.008	10.692	1.049	1.007	15.101	32.434	77.630	-0.7
e5c	77.100	5.019	1.380	1.004	10.643	1.029	1.002	7.715	23.890	79.997	-1.0
e5d	76.300	10.482	1.363	1.003	10.943	1.039	1.016	15.100	37.777	77.907	-1.3
e5e	60.100	5.108	1.385	1.020	10.747	1.008	1.039	15.000	33.085	60.835	-1.6
e6a	14.400	2.353	1.246	0.934	7.963	0.921	0.926	7.158	21.892	13.878	-0.4
e6b	28.300	4.538	0.819	0.649	6.419	0.597	0.630	13.600	25.691	28.595	-2.3

Table A8.2. Equilibrium Mass of Hexane(1), Water(2), Mesitylene(3), 5-Et-2-me-pyridine(4), Aniline(5), Benzonitrile(6), Phenol(7) and TEG monomethylether(8) in Solvent and Antisolvent Phase for Batch Extractions using the Phenol Feed Stream at 313.15K

Exp.	Masses of Components in Solvent Phase [g]								ε_{SP}	Masses of Components in Antisolvent Phase [g]								ε_{HP}	Mass Balance Errors over Components [%]							
ID	m_1^I	m_2^I	m_3^I	m_4^I	m_5^I	m_6^I	m_7^I	m_8^I	[%]	m_1^{II}	m_2^{II}	m_3^{II}	m_4^{II}	m_5^{II}	m_6^{II}	m_7^{II}	m_8^{II}	[%]	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	ε_7	ε_8
e1a	0.867	9.951	0.136	0.919	10.781	0.770	0.654	29.809	-0.5	44.385	0.014	1.580	0.073	0.287	0.248	0.396	0.182	0.1	-2.3	-0.4	-2.5	-1.5	0.1	-1.7	0.1	-1.9
e1b	0.437	20.291	0.058	0.898	10.298	0.675	0.533	30.524	1.0	45.620	0.012	1.351	0.095	0.376	0.306	0.464	0.144	1.1	-0.1	-0.8	0.4	-1.7	0.0	-2.5	-0.9	1.1
e1c	1.019	4.883	0.100	0.892	10.472	0.717	0.634	15.010	2.6	44.278	0.012	1.331	0.111	0.471	0.291	0.441	0.083	-0.7	-2.0	-2.3	0.3	-2.9	-0.4	-0.1	2.8	-2.2
e1d	0.756	9.866	0.073	0.935	10.766	0.799	0.593	29.461	0.2	73.918	0.017	1.293	0.100	0.408	0.374	0.545	0.237	2.2	-0.4	-1.8	-0.7	2.4	2.4	-0.1	1.6	-1.8
e1e	0.575	21.032	0.028	0.902	10.368	0.599	0.453	29.806	1.7	78.943	0.019	1.359	0.143	0.536	0.433	0.638	0.126	-0.4	5.9	2.6	0.8	-2.5	2.4	-1.4	-0.6	-2.0
e2a	1.448	15.459	0.116	0.922	10.750	0.793	0.626	46.011	0.9	44.039	0.013	1.295	0.063	0.302	0.193	0.380	0.059	-1.2	-2.6	2.9	1.3	-3.1	1.6	-3.4	-0.9	-0.1
e2b	0.596	29.498	0.053	0.944	10.384	0.731	0.583	44.750	-0.3	44.024	0.017	1.326	0.074	0.335	0.271	0.448	0.049	-3.2	-3.8	-3.0	-1.1	-1.3	-1.8	-1.4	1.2	-0.6
e2c	4.718	5.076	0.284	0.970	10.460	0.842	0.744	44.197	3.4	42.597	0.011	1.116	0.037	0.169	0.130	0.277	0.545	0.2	3.3	1.0	-0.9	0.3	-2.2	-3.2	0.7	-2.4
e2d	0.519	29.545	0.037	0.856	10.074	0.611	0.499	22.969	0.6	45.489	0.020	1.367	0.138	0.752	0.437	0.770	0.067	3.2	-1.5	-1.9	0.7	-1.3	0.0	1.0	2.0	1.0
e2e	0.633	14.794	0.055	0.904	10.241	0.660	0.535	22.504	0.7	45.552	0.015	1.292	0.116	0.467	0.330	0.516	0.093	0.0	-2.8	-1.8	0.9	-1.1	-0.3	-1.3	4.0	0.0
e3a	0.918	1.695	0.068	0.441	5.208	0.364	0.310	7.649	1.7	21.016	0.004	0.590	0.052	0.222	0.141	0.203	0.112	-1.2	-2.9	0.2	-1.5	-1.8	-2.3	-2.5	1.5	0.0
e3b	0.587	2.679	0.049	0.457	5.248	0.349	0.288	7.378	-1.1	22.120	0.005	0.642	0.057	0.247	0.143	0.214	0.045	2.9	0.5	-1.2	1.5	0.1	-0.7	-3.2	0.2	-2.2
e3c	0.339	5.198	0.033	0.448	4.963	0.344	0.261	7.435	1.0	22.592	0.006	0.669	0.063	0.312	0.174	0.262	0.020	2.7	1.9	-2.0	0.9	-0.9	-2.5	-2.0	1.7	-2.0
e3d	0.566	5.124	0.042	0.478	5.377	0.377	0.306	15.291	1.1	29.661	0.006	0.684	0.037	0.169	0.146	0.232	0.108	1.0	-1.5	-1.9	1.6	-1.0	2.9	1.2	3.4	1.8
e3e	0.530	3.260	0.041	0.456	5.264	0.335	0.285	9.998	0.9	29.550	0.006	0.646	0.059	0.245	0.157	0.256	0.107	0.0	-2.7	-1.7	1.0	1.1	2.9	-1.7	0.2	-2.0
e4a	2.021	0.757	0.185	0.852	9.869	0.707	0.620	7.837	4.2	42.362	0.012	1.196	0.161	0.878	0.286	0.411	0.235	0.0	-1.4	-1.5	-0.6	-0.5	0.0	-3.3	1.5	1.5
e4b	1.433	2.597	0.116	0.852	9.547	0.655	0.564	7.442	2.8	46.245	0.014	1.343	0.162	0.858	0.331	0.488	0.110	1.1	1.4	1.9	0.9	-0.6	-2.1	-1.6	2.3	-2.6
e4c	0.917	4.922	0.080	0.859	9.855	0.664	0.587	7.535	2.3	42.674	0.015	1.289	0.169	0.940	0.366	0.558	0.046	-2.7	-3.5	-2.2	0.8	-1.6	1.1	-2.7	5.4	-0.5
e4d	2.013	2.570	0.165	0.968	10.358	0.779	0.721	7.769	3.5	28.502	0.010	1.208	0.106	0.575	0.245	0.357	0.077	4.2	-0.3	0.5	0.5	1.4	2.0	0.5	1.8	-0.1
e4e	1.739	2.530	0.083	0.801	9.612	0.621	0.508	7.365	1.6	56.678	0.018	1.365	0.193	0.998	0.382	0.519	0.113	-0.7	-3.6	-0.3	1.7	-1.4	-2.0	-1.4	0.8	-1.1
e5a	1.441	2.557	0.079	0.808	9.383	0.578	0.474	8.574	1.9	73.684	0.019	1.464	0.219	1.113	0.435	0.569	0.107	2.8	0.0	0.6	-1.0	-1.7	-2.7	-0.3	3.7	1.1
e5b	1.281	4.930	0.073	0.846	9.932	0.632	0.482	15.054	2.5	74.605	0.018	1.340	0.156	0.638	0.406	0.554	0.163	0.3	0.5	-1.3	-2.7	-0.7	-1.1	-1.0	2.9	0.8
e5c	0.747	4.921	0.040	0.745	9.549	0.507	0.388	7.732	3.1	75.811	0.024	1.355	0.254	1.333	0.503	0.615	0.076	0.0	-0.7	-1.5	1.1	-0.5	2.2	-1.9	0.1	1.2
e5d	0.583	10.351	0.028	0.829	9.849	0.517	0.431	15.324	0.4	76.575	0.019	1.336	0.187	0.931	0.486	0.597	0.152	3.1	1.1	-1.1	0.1	1.3	-1.5	-3.5	1.1	2.5
e5e	0.932	5.095	0.072	0.838	10.301	0.628	0.554	15.472	2.4	56.889	0.015	1.300	0.153	0.655	0.365	0.509	0.174	-1.3	-3.8	0.1	-0.9	-2.8	1.9	-1.5	2.4	4.3
e6a	1.548	2.299	0.351	0.892	7.727	0.809	0.764	7.150	-1.6	12.561	0.006	0.909	0.050	0.290	0.102	0.162	0.012	1.6	-2.0	-2.0	1.1	0.9	0.7	-1.1	0.0	0.1
e6b	1.184	4.496	0.068	0.578	6.097	0.432	0.353	13.443	3.7	27.081	0.008	0.756	0.061	0.205	0.166	0.276	0.098	0.2	-0.1	-0.7	0.6	-1.4	-1.8	0.2	-0.2	-0.4

APPENDIX B: STOICHIOMETRIC MASSES FOR SYNTHESIS OF SOLVENTS

Table B1. Stoichiometric masses for synthesis Ethylene Glycol Derivative

	Ethylene Glycol (EG)	Sodium	EG sodium salt	Hydrogen gas	1,3-dichloro-propane-2-ol	EG derivative	Water	Sodium Hydroxide	Hydrochloric Acid	Sodium Chloride
Mass Added[g]	**44.8.6**	**9.8**	-	-	-	-	-	-	-	-
$n_{in\ mixture}$	4.23	0.43	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$n_{reacted}$	0.43	0.43	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
n_{formed}	0.0	0.0	0.43	0.215	0.0	0.0	0.0	0.0	0.0	0.0
$n_{remaining}$	3.80	0.0	0.43	0.215	0.0	0.0	0.0	0.0	0.0	0.0
Mass Added[g]	-	-	-	**-0.430**	**16.91**	-	-	-	-	-
$n_{in\ mixture}$	3.80	0.0	0.43	0.0	0.131	0.0	0.0	0.0	0.0	0.0
$n_{reacted}$	0.0	0.0	0.262	0.0	0.131	0.0	0.0	0.0	0.0	0.0
n_{formed}	0.0	0.0	0.0	0.0	0.0	0.131	0.0	0.0	0.0	0.262
$n_{remaining}$	3.80	0.0	0.168	0.0	0.0	0.131	0.0	0.0	0.0	0.262
Mass Added[g]	-	-	-	-	-	-	**9.377**	-	-	-
$n_{in\ mixture}$	3.80	0.0	0.168	0.0	0.0	0.131	0.521	0.0	0.0	0.262
$n_{reacted}$	0.0	0.00	0.168	0.00	0.00	0.0	0.168	0.0	0.0	0.0
n_{formed}	0.168	0.0	0.0	0.0	0.0	0.0	0.0	0.168	0.0	0.0
$n_{remaining}$	3.968	0.0	0.0	0.0	0.0	0.131	0.353	0.168	0.0	0.262
Mass Added[g]	-	-	-	-	-	-	**16.89**	-	**7.24**	-
$n_{in\ mixture}$	3.968	0.0	0.0	0.0	0.0	0.131	1.292	0.168	0.201	0.262
$n_{reacted}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.168	0.168	0
n_{formed}	0.0	0.0	0.0	0.0	0.0	0.0	0.168	0.0	0.0	0.168
$n_{remaining}$	3.968	0.0	0.0	0.0	0.0	0.131	1.46	0.0	0.033	0.430
Mass Out [g]	**420.6**	**0.0**	**0.0**	**0.0**	**0.0**	**23.58**	**26.28**	**0.0**	**1.180**	**24.94**

Table B2. Stoichiometric masses for synthesis of Diethylene Glycol Derivative

	Diethylene Glycol (DiEG)	Sodium	DiEG sodium salt	Hydrogen gas	1,3-dichloro-propane-2-ol	DiEG derivative	Water	Sodium Hydroxide	Hydrochloric Acid	Sodium Chloride
Mass Added[g]	**454.7**	**23.28**	-	-	-	-	-	-	-	-
$n_{in\ mixture}$	4.29	0.596	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$n_{reacted}$	0.596	0.596	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
n_{formed}	0.0	0.0	0.596	0.298	0.0	0.0	0.0	0.0	0.0	0.0
$n_{remaining}$	3.69	0.0	0.596	0.298	0.0	0.0	0.0	0.0	0.0	0.0
Mass Added[g]	-	-	-	**-0.596**	**23.1**	-	-	-	-	-
$n_{in\ mixture}$	3.69	0.0	0.596	0.0	0.179	0.0	0.0	0.0	0.0	0.0
$n_{reacted}$	0.0	0.0	0.358	0.0	0.179	0.0	0.0	0.0	0.0	0.0
n_{formed}	0.0	0.0	0.0	0.0	0.0	0.179	0.0	0.0	0.0	0.358
$n_{remaining}$	3.69	0.0	0.238	0.0	0.0	0.179	0.0	0.0	0.0	0.358
Mass Added[g]	-	-	-	-	-	-	**13.276**	-	-	-
$n_{in\ mixture}$	3.69	0.0	0.238	0.0	0.0	0.179	0.737	0.0	0.0	0.358
$n_{reacted}$	0.0	0.00	0.238	0.00	0.00	0.0	0.238	0.0	0.0	0.0
n_{formed}	0.238	0.0	0.0	0.0	0.0	0.0	0.0	0.238	0.0	0.0
$n_{remaining}$	3.93	0.0	0.0	0.0	0.0	0.179	0.499	0.238	0.0	0.358
Mass Added[g]	-	-	-	-	-	-	**21.211**	-	**9.09**	-
$n_{in\ mixture}$	3.93	0.0	0.0	0.0	0.0	0.179	1.677	0.238	0.249	0.358
$n_{reacted}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.238	0.238	0
n_{formed}	0.0	0.0	0.0	0.0	0.0	0.0	0.238	0.0	0.0	0.238
$n_{remaining}$	0.0	0.0	0.0	0.0	0.0	0.179	1.915	0.0	0.011	0.596
Mass Out [g]	416.6	0.0	0.0	0.0	0.0	48.0	34.5	0.0	0.400	34..8

APPENDIX C: PREDICTED AND EXPERIMENTAL MOLAR FRACTIONS

Table C1: Simulated and experimental equilibrium molar fractions of the extract phase, x^{I}_{i} and raffinate phase, x^{II}_{i}, for the system Hexane(1) + Water(2) + Mesitylene(3) + 5-Ethyl-2-methyl pyridine(4) + Aniline(5) + Benzonitrile(6) + Phenol(7) + Triethylene Glycol(8)

ID	sim.	x^{I}_{1}	x^{I}_{2}	x^{I}_{3}	x^{I}_{4}	x^{I}_{5}	x^{I}_{6}	x^{I}_{7}	x^{I}_{8}	x^{II}_{1}	x^{II}_{2}	x^{II}_{3}	x^{II}_{4}	x^{II}_{5}	x^{II}_{6}	x^{II}_{7}	x^{II}_{8}
1A	**exp.**	**0.0083**	**0.5437**	**0.0010**	**0.0079**	**0.0184**	**0.0127**	**0.2090**	**0.1991**	**0.9423**	**0.0021**	**0.0209**	**0.0089**	**0.0031**	**0.0075**	**0.0134**	**0.0019**
1A	sim.	0.0075	0.5480	0.0007	0.0076	0.0182	0.0124	0.2090	0.1966	0.9483	0.0010	0.0200	0.0081	0.0029	0.0070	0.0126	0.0000
1B	**exp.**	**0.0111**	**0.5328**	**0.0029**	**0.0115**	**0.0198**	**0.0162**	**0.2143**	**0.1915**	**0.8969**	**0.0026**	**0.0535**	**0.0132**	**0.0038**	**0.0102**	**0.0191**	**0.0007**
1B	sim.	0.0081	0.5368	0.0022	0.0113	0.0195	0.0155	0.2129	0.1938	0.9008	0.0013	0.0540	0.0126	0.0037	0.0095	0.0180	0.0000
1C	**exp.**	**0.0115**	**0.5285**	**0.0048**	**0.0124**	**0.0195**	**0.0171**	**0.2104**	**0.1959**	**0.8504**	**0.0019**	**0.0867**	**0.0177**	**0.0047**	**0.0126**	**0.0254**	**0.0006**
1C	sim.	0.0079	0.5338	0.0041	0.0129	0.0198	0.0166	0.2129	0.1920	0.8485	0.0019	0.0917	0.0152	0.0045	0.0120	0.0262	0.0001
1D	**exp.**	**0.0023**	**0.7655**	**0.0001**	**0.0021**	**0.0080**	**0.0039**	**0.0890**	**0.1291**	**0.9585**	**0.0008**	**0.0120**	**0.0068**	**0.0030**	**0.0065**	**0.0116**	**0.0008**
1D	sim.	0.0008	0.7609	0.0001	0.0020	0.0081	0.0038	0.0901	0.1343	0.9582	0.0010	0.0123	0.0068	0.0029	0.0063	0.0124	0.0000
2A	**exp.**	**0.0090**	**0.5527**	**0.0006**	**0.0056**	**0.0174**	**0.0106**	**0.2051**	**0.1990**	**0.9625**	**0.0016**	**0.0126**	**0.0062**	**0.0024**	**0.0051**	**0.0097**	**0.0000**
2A	sim.	0.0070	0.5547	0.0004	0.0058	0.0170	0.0099	0.2055	0.1997	0.9604	0.0009	0.0128	0.0062	0.0026	0.0056	0.0115	0.0000
2B	**exp.**	**0.0040**	**0.7124**	**0.0011**	**0.0064**	**0.0121**	**0.0095**	**0.1333**	**0.1212**	**0.8829**	**0.0022**	**0.0569**	**0.0158**	**0.0043**	**0.0128**	**0.0249**	**0.0001**
2B	sim.	0.0026	0.7045	0.0009	0.0060	0.0126	0.0092	0.1374	0.1269	0.8794	0.0017	0.0562	0.0184	0.0049	0.0146	0.0248	0.0000
2C	**exp.**	**0.0049**	**0.6973**	**0.0023**	**0.0073**	**0.0126**	**0.0105**	**0.1381**	**0.1271**	**0.8148**	**0.0032**	**0.0985**	**0.0239**	**0.0070**	**0.0167**	**0.0357**	**0.0001**
2C	sim.	0.0025	0.7026	0.0017	0.0067	0.0127	0.0094	0.1379	0.1266	0.8008	0.0027	0.0978	0.0284	0.0070	0.0224	0.0407	0.0001
2D	**exp.**	**0.0036**	**0.7112**	**0.0005**	**0.0042**	**0.0114**	**0.0072**	**0.1338**	**0.1281**	**0.9378**	**0.0029**	**0.0211**	**0.0095**	**0.0034**	**0.0080**	**0.0161**	**0.0011**
2D	sim.	0.0023	0.7133	0.0003	0.0039	0.0116	0.0068	0.1338	0.1282	0.9410	0.0012	0.0201	0.0095	0.0035	0.0084	0.0161	0.0000
3A	**exp.**	**0.0098**	**0.5928**	**0.0057**	**0.0129**	**0.0205**	**0.0180**	**0.2378**	**0.1025**	**0.8056**	**0.0043**	**0.0954**	**0.0240**	**0.0086**	**0.0155**	**0.0463**	**0.0002**
3A	sim.	0.0115	0.5934	0.0028	0.0136	0.0215	0.0175	0.2326	0.1070	0.8127	0.0032	0.0979	0.0196	0.0068	0.0153	0.0445	0.0000
3B	**exp.**	**0.0020**	**0.7457**	**0.0012**	**0.0052**	**0.0088**	**0.0071**	**0.0977**	**0.1324**	**0.8114**	**0.0032**	**0.0993**	**0.0256**	**0.0070**	**0.0188**	**0.0345**	**0.0003**
3B	sim.	0.0010	0.7452	0.0013	0.0045	0.0091	0.0068	0.0980	0.1341	0.8119	0.0022	0.0948	0.0308	0.0060	0.0210	0.0332	0.0001
3C	**exp.**	**0.0012**	**0.7632**	**0.0008**	**0.0039**	**0.0071**	**0.0061**	**0.0773**	**0.1404**	**0.8077**	**0.0026**	**0.1059**	**0.0271**	**0.0048**	**0.0207**	**0.0309**	**0.0003**
3C	sim.	0.0005	0.7671	0.0011	0.0036	0.0072	0.0059	0.0763	0.1381	0.8178	0.0020	0.0939	0.0292	0.0053	0.0235	0.0283	0.0001
3D	**exp.**	**0.0006**	**0.7946**	**0.0005**	**0.0029**	**0.0049**	**0.0040**	**0.0531**	**0.1395**	**0.8187**	**0.0030**	**0.1102**	**0.0245**	**0.0034**	**0.0164**	**0.0236**	**0.0004**
3D	sim.	0.0002	0.7922	0.0010	0.0028	0.0049	0.0040	0.0527	0.1423	0.8431	0.0017	0.0936	0.0247	0.0036	0.0132	0.0202	0.0000
4A	**exp.**	**0.0065**	**0.6198**	**0.0010**	**0.0073**	**0.0196**	**0.0129**	**0.2233**	**0.1097**	**0.9327**	**0.0025**	**0.0203**	**0.0099**	**0.0037**	**0.0081**	**0.0225**	**0.0003**
4A	sim.	0.0108	0.6132	0.0004	0.0075	0.0191	0.0126	0.2266	0.1097	0.9395	0.0014	0.0201	0.0091	0.0038	0.0077	0.0184	0.0000
4B	**exp.**	**0.0016**	**0.7576**	**0.0002**	**0.0027**	**0.0080**	**0.0052**	**0.0920**	**0.1326**	**0.9435**	**0.0017**	**0.0199**	**0.0100**	**0.0029**	**0.0078**	**0.0141**	**0.0002**
4B	sim.	0.0010	0.7517	0.0002	0.0028	0.0083	0.0051	0.0955	0.1355	0.9436	0.0011	0.0202	0.0095	0.0031	0.0086	0.0139	0.0000
4C	**exp.**	**0.0011**	**0.7777**	**0.0002**	**0.0021**	**0.0067**	**0.0042**	**0.0724**	**0.1357**	**0.9402**	**0.0017**	**0.0213**	**0.0109**	**0.0030**	**0.0083**	**0.0139**	**0.0006**
4C	sim.	0.0005	0.7732	0.0002	0.0022	0.0069	0.0040	0.0742	0.1388	0.9467	0.0010	0.0201	0.0094	0.0028	0.0079	0.0120	0.0000
4D	**exp.**	**0.0016**	**0.7993**	**0.0001**	**0.0015**	**0.0047**	**0.0030**	**0.0510**	**0.1388**	**0.9445**	**0.0014**	**0.0221**	**0.0101**	**0.0026**	**0.0084**	**0.0107**	**0.0002**
4D	sim.	0.0002	0.7952	0.0002	0.0017	0.0048	0.0031	0.0516	0.1432	0.9512	0.0010	0.0202	0.0088	0.0022	0.0073	0.0093	0.0000
5A	**exp.**	**0.0066**	**0.2863**	**0.0071**	**0.0183**	**0.0307**	**0.0252**	**0.3312**	**0.2946**	**0.9005**	**0.0020**	**0.0547**	**0.0114**	**0.0036**	**0.0092**	**0.0182**	**0.0005**
5A	sim.	0.0222	0.2717	0.0069	0.0194	0.0309	0.0251	0.3271	0.2967	0.9109	0.0008	0.0512	0.0099	0.0031	0.0077	0.0162	0.0001
5B	**exp.**	**0.0056**	**0.2902**	**0.0114**	**0.0214**	**0.0318**	**0.0270**	**0.3273**	**0.2853**	**0.8545**	**0.0047**	**0.0901**	**0.0135**	**0.0039**	**0.0105**	**0.0221**	**0.0007**
5B	sim.	0.0218	0.2708	0.0119	0.0212	0.0310	0.0259	0.3241	0.2934	0.8718	0.0010	0.0819	0.0113	0.0036	0.0090	0.0214	0.0001

Table C1 (cont.)

ID	sim.	x'_1	x'_2	x'_3	x'_4	x'_5	x'_6	x'_7	x'_8	x''_1	x''_2	x''_3	x''_4	x''_5	x''_6	x''_7	x''_8
5C	**exp.**	**0.0115**	**0.3323**	**0.0020**	**0.0107**	**0.0218**	**0.0162**	**0.2517**	**0.3538**	**0.9542**	**0.0015**	**0.0189**	**0.0074**	**0.0022**	**0.0058**	**0.0096**	**0.0004**
5C	sim.	0.0110	0.3250	0.0019	0.0110	0.0228	0.0165	0.2571	0.3548	0.9571	0.0005	0.0195	0.0068	0.0021	0.0057	0.0083	0.0001
5D	**exp.**	**0.0208**	**0.2883**	**0.0014**	**0.0101**	**0.0273**	**0.0178**	**0.3282**	**0.3060**	**0.9625**	**0.0010**	**0.0121**	**0.0055**	**0.0026**	**0.0051**	**0.0108**	**0.0004**
5D	sim.	0.0198	0.2877	0.0015	0.0106	0.0281	0.0174	0.3229	0.3121	0.9637	0.0006	0.0122	0.0055	0.0024	0.0050	0.0106	0.0000
6A	**exp.**	**0.0412**	**0.2076**	**0.0033**	**0.0175**	**0.0365**	**0.0268**	**0.4536**	**0.2134**	**0.9433**	**0.0011**	**0.0182**	**0.0071**	**0.0033**	**0.0066**	**0.0201**	**0.0004**
6A	sim.	0.0536	0.1988	0.0037	0.0178	0.0369	0.0273	0.4493	0.2125	0.9465	0.0007	0.0179	0.0070	0.0032	0.0061	0.0187	0.0000
6B	**exp.**	**0.0208**	**0.2848**	**0.0027**	**0.0138**	**0.0293**	**0.0209**	**0.3264**	**0.3013**	**0.9530**	**0.0008**	**0.0189**	**0.0070**	**0.0026**	**0.0059**	**0.0114**	**0.0003**
6B	sim.	0.0212	0.2784	0.0024	0.0139	0.0296	0.0209	0.3272	0.3064	0.9528	0.0006	0.0193	0.0071	0.0026	0.0060	0.0116	0.0000
6C	**exp.**	**0.0110**	**0.3513**	**0.0021**	**0.0090**	**0.0189**	**0.0130**	**0.2167**	**0.3780**	**0.9551**	**0.0007**	**0.0190**	**0.0074**	**0.0024**	**0.0060**	**0.0091**	**0.0003**
6C	sim.	0.0066	0.3578	0.0015	0.0092	0.0192	0.0134	0.2108	0.3814	0.9600	0.0005	0.0194	0.0066	0.0018	0.0053	0.0063	0.0001
6D	**exp.**	**0.0099**	**0.3866**	**0.0019**	**0.0074**	**0.0141**	**0.0101**	**0.1557**	**0.4145**	**0.9636**	**0.0009**	**0.0189**	**0.0060**	**0.0014**	**0.0044**	**0.0048**	**0.0000**
6D	sim.	0.0033	0.3884	0.0012	0.0073	0.0143	0.0101	0.1555	0.4198	0.9637	0.0005	0.0192	0.0063	0.0014	0.0047	0.0041	0.0001
7A	**exp.**	**0.0131**	**0.6298**	**0.0006**	**0.0059**	**0.0173**	**0.0109**	**0.2137**	**0.1086**	**0.9525**	**0.0012**	**0.0125**	**0.0064**	**0.0035**	**0.0063**	**0.0173**	**0.0003**
7A	sim.	0.0099	0.6225	0.0003	0.0053	0.0179	0.0102	0.2222	0.1118	0.9534	0.0013	0.0123	0.0065	0.0035	0.0063	0.0168	0.0000
7B	**exp.**	**0.0053**	**0.7160**	**0.0003**	**0.0029**	**0.0106**	**0.0056**	**0.1310**	**0.1284**	**0.9581**	**0.0011**	**0.0124**	**0.0067**	**0.0029**	**0.0061**	**0.0125**	**0.0001**
7B	sim.	0.0022	0.7173	0.0002	0.0029	0.0107	0.0053	0.1323	0.1292	0.9560	0.0011	0.0122	0.0067	0.0030	0.0063	0.0146	0.0000
7C	**exp.**	**0.0033**	**0.7759**	**0.0001**	**0.0016**	**0.0061**	**0.0031**	**0.0717**	**0.1382**	**0.9603**	**0.0009**	**0.0126**	**0.0067**	**0.0027**	**0.0062**	**0.0106**	**0.0001**
7C	sim.	0.0005	0.7741	0.0001	0.0017	0.0062	0.0032	0.0729	0.1413	0.9613	0.0010	0.0124	0.0066	0.0024	0.0058	0.0106	0.0000
7D	**exp.**	**0.0018**	**0.7982**	**0.0001**	**0.0013**	**0.0044**	**0.0023**	**0.0494**	**0.1425**	**0.9662**	**0.0006**	**0.0116**	**0.0064**	**0.0021**	**0.0056**	**0.0074**	**0.0002**
7D	sim.	0.0002	0.7981	0.0001	0.0013	0.0045	0.0024	0.0503	0.1430	0.9647	0.0009	0.0122	0.0066	0.0020	0.0053	0.0084	0.0000
8A	**exp.**	**0.0123**	**0.6047**	**0.0031**	**0.0120**	**0.0206**	**0.0160**	**0.2254**	**0.1059**	**0.8840**	**0.0033**	**0.0513**	**0.0137**	**0.0047**	**0.0109**	**0.0319**	**0.0002**
8A	sim.	0.0120	0.5966	0.0014	0.0118	0.0211	0.0165	0.2335	0.1072	0.8839	0.0020	0.0556	0.0150	0.0051	0.0109	0.0276	0.0000
8B	**exp.**	**0.0030**	**0.7424**	**0.0007**	**0.0046**	**0.0096**	**0.0068**	**0.0990**	**0.1339**	**0.8879**	**0.0020**	**0.0522**	**0.0175**	**0.0043**	**0.0123**	**0.0235**	**0.0003**
8B	sim.	0.0010	0.7459	0.0006	0.0042	0.0094	0.0064	0.0983	0.1341	0.8870	0.0015	0.0538	0.0191	0.0044	0.0134	0.0208	0.0000
8C	**exp.**	**0.0023**	**0.7891**	**0.0004**	**0.0030**	**0.0064**	**0.0047**	**0.0689**	**0.1253**	**0.8924**	**0.0013**	**0.0517**	**0.0171**	**0.0037**	**0.0125**	**0.0210**	**0.0003**
8C	sim.	0.0004	0.7889	0.0004	0.0028	0.0064	0.0046	0.0694	0.1270	0.8945	0.0014	0.0506	0.0184	0.0037	0.0129	0.0183	0.0000
8D	**exp.**	**0.0026**	**0.7936**	**0.0004**	**0.0027**	**0.0051**	**0.0039**	**0.0522**	**0.1395**	**0.8747**	**0.0017**	**0.0691**	**0.0189**	**0.0033**	**0.0133**	**0.0187**	**0.0003**
8D	sim.	0.0002	0.7924	0.0005	0.0025	0.0051	0.0037	0.0531	0.1425	0.9021	0.0012	0.0532	0.0166	0.0029	0.0103	0.0136	0.0000
8E	**exp.**	**0.0013**	**0.7980**	**0.0003**	**0.0025**	**0.0049**	**0.0037**	**0.0503**	**0.1390**	**0.8910**	**0.0015**	**0.0555**	**0.0172**	**0.0030**	**0.0118**	**0.0160**	**0.0040**
8E	sim.	0.0002	0.7926	0.0005	0.0025	0.0051	0.0038	0.0526	0.1427	0.9031	0.0012	0.0522	0.0168	0.0029	0.0105	0.0134	0.0000
9A	**exp.**	**0.0252**	**0.4393**	**0.0020**	**0.0128**	**0.0300**	**0.0201**	**0.3189**	**0.1517**	**0.9406**	**0.0015**	**0.0199**	**0.0075**	**0.0035**	**0.0069**	**0.0196**	**0.0004**
9A	sim.	0.0261	0.4296	0.0013	0.0127	0.0304	0.0202	0.3236	0.1560	0.9428	0.0012	0.0207	0.0078	0.0038	0.0066	0.0171	0.0000
9B	**exp.**	**0.0065**	**0.6103**	**0.0007**	**0.0057**	**0.0140**	**0.0091**	**0.1468**	**0.2069**	**0.9496**	**0.0010**	**0.0208**	**0.0080**	**0.0027**	**0.0068**	**0.0109**	**0.0002**
9B	sim.	0.0017	0.6350	0.0005	0.0044	0.0107	0.0069	0.1174	0.2235	0.9535	0.0009	0.0203	0.0082	0.0022	0.0066	0.0084	0.0000
9C	**exp.**	**0.0044**	**0.6325**	**0.0004**	**0.0046**	**0.0109**	**0.0072**	**0.1184**	**0.2216**	**0.9514**	**0.0008**	**0.0213**	**0.0083**	**0.0025**	**0.0064**	**0.0093**	**0.0001**
9C	sim.	0.0017	0.6350	0.0005	0.0044	0.0107	0.0069	0.1174	0.2235	0.9535	0.0009	0.0203	0.0082	0.0022	0.0066	0.0084	0.0000

Table C1 (cont.)

ID	sim.	x'_1	x'_2	x'_3	x'_4	x'_5	x'_6	x'_7	x'_8	x''_1	x''_2	x''_3	x''_4	x''_5	x''_6	x''_7	x''_8
9D	**exp.**	**0.0056**	**0.6566**	**0.0004**	**0.0036**	**0.0081**	**0.0056**	**0.0860**	**0.2342**	**0.9557**	**0.0005**	**0.0208**	**0.0076**	**0.0018**	**0.0058**	**0.0061**	**0.0017**
9D	sim.	0.0009	0.6608	0.0004	0.0034	0.0079	0.0052	0.0865	0.2350	0.9575	0.0008	0.0199	0.0077	0.0018	0.0059	0.0065	0.0000
10A	**exp.**	**0.0069**	**0.5997**	**0.0019**	**0.0082**	**0.0145**	**0.0119**	**0.1513**	**0.2056**	**0.9013**	**0.0012**	**0.0537**	**0.0133**	**0.0034**	**0.0102**	**0.0163**	**0.0006**
10A	sim.	0.0036	0.5921	0.0017	0.0084	0.0151	0.0116	0.1565	0.2111	0.9039	0.0012	0.0537	0.0134	0.0033	0.0099	0.0145	0.0000
10B	**exp.**	**0.0171**	**0.4378**	**0.0060**	**0.0197**	**0.0310**	**0.0251**	**0.3134**	**0.1501**	**0.8903**	**0.0019**	**0.0510**	**0.0131**	**0.0051**	**0.0101**	**0.0277**	**0.0007**
10B	sim.	0.0264	0.4231	0.0036	0.0203	0.0320	0.0250	0.3190	0.1506	0.8932	0.0016	0.0545	0.0124	0.0048	0.0090	0.0246	0.0000
10C	**exp.**	**0.0064**	**0.6235**	**0.0013**	**0.0069**	**0.0111**	**0.0090**	**0.1190**	**0.2227**	**0.9065**	**0.0012**	**0.0550**	**0.0130**	**0.0026**	**0.0086**	**0.0125**	**0.0005**
10C	sim.	0.0020	0.6217	0.0014	0.0068	0.0116	0.0091	0.1245	0.2231	0.9078	0.0011	0.0534	0.0135	0.0028	0.0093	0.0120	0.0000
10D	**exp.**	**0.0030**	**0.6513**	**0.0011**	**0.0052**	**0.0085**	**0.0065**	**0.0890**	**0.2354**	**0.9047**	**0.0010**	**0.0611**	**0.0125**	**0.0021**	**0.0082**	**0.0100**	**0.0004**
10D	sim.	0.0010	0.6525	0.0012	0.0050	0.0087	0.0065	0.0905	0.2346	0.9125	0.0010	0.0546	0.0124	0.0023	0.0079	0.0093	0.0000
11A	**exp.**	**0.0081**	**0.5953**	**0.0034**	**0.0099**	**0.0150**	**0.0127**	**0.1531**	**0.2026**	**0.8455**	**0.0015**	**0.1016**	**0.0165**	**0.0037**	**0.0116**	**0.0194**	**0.0002**
11A	sim.	0.0034	0.5903	0.0031	0.0094	0.0149	0.0121	0.1560	0.2105	0.8554	0.0016	0.0901	0.0165	0.0039	0.0120	0.0204	0.0001
11B	**exp.**	**0.0129**	**0.4233**	**0.0102**	**0.0207**	**0.0314**	**0.0273**	**0.3224**	**0.1517**	**0.8537**	**0.0023**	**0.0826**	**0.0132**	**0.0051**	**0.0108**	**0.0321**	**0.0002**
11B	sim.	0.0274	0.4137	0.0070	0.0210	0.0307	0.0265	0.3256	0.1480	0.8364	0.0024	0.0934	0.0134	0.0056	0.0112	0.0377	0.0000
11C	**exp.**	**0.0074**	**0.6206**	**0.0024**	**0.0075**	**0.0120**	**0.0099**	**0.1214**	**0.2188**	**0.8556**	**0.0013**	**0.0968**	**0.0154**	**0.0032**	**0.0112**	**0.0165**	**0.0000**
11C	sim.	0.0019	0.6198	0.0028	0.0074	0.0120	0.0097	0.1244	0.2220	0.8603	0.0014	0.0905	0.0160	0.0034	0.0114	0.0170	0.0001
11D	**exp.**	**0.0053**	**0.6584**	**0.0017**	**0.0055**	**0.0084**	**0.0070**	**0.0871**	**0.2266**	**0.8408**	**0.0011**	**0.1172**	**0.0147**	**0.0025**	**0.0098**	**0.0134**	**0.0004**
11D	sim.	0.0009	0.6532	0.0022	0.0054	0.0085	0.0069	0.0882	0.2348	0.8728	0.0012	0.0871	0.0145	0.0026	0.0096	0.0121	0.0001
12A	**exp.**	**0.0220**	**0.3241**	**0.0053**	**0.0151**	**0.0248**	**0.0195**	**0.2536**	**0.3356**	**0.9179**	**0.0007**	**0.0491**	**0.0103**	**0.0027**	**0.0076**	**0.0114**	**0.0004**
12A	sim.	0.0111	0.3224	0.0050	0.0150	0.0249	0.0193	0.2550	0.3472	0.9203	0.0007	0.0488	0.0095	0.0026	0.0071	0.0110	0.0001
12B	**exp.**	**0.0121**	**0.3577**	**0.0044**	**0.0126**	**0.0207**	**0.0184**	**0.2037**	**0.3706**	**0.9216**	**0.0008**	**0.0493**	**0.0098**	**0.0022**	**0.0071**	**0.0090**	**0.0002**
12B	sim.	0.0068	0.3545	0.0041	0.0125	0.0202	0.0176	0.2097	0.3746	0.9237	0.0006	0.0483	0.0093	0.0022	0.0074	0.0084	0.0001
12C	**exp.**	**0.0498**	**0.2084**	**0.0094**	**0.0261**	**0.0404**	**0.0340**	**0.4285**	**0.2034**	**0.8974**	**0.0015**	**0.0500**	**0.0104**	**0.0046**	**0.0093**	**0.0263**	**0.0004**
12C	sim.	0.0536	0.2005	0.0101	0.0255	0.0398	0.0334	0.4326	0.2045	0.9018	0.0009	0.0493	0.0102	0.0041	0.0082	0.0255	0.0001
12D	**exp.**	**0.0097**	**0.3900**	**0.0037**	**0.0098**	**0.0144**	**0.0122**	**0.1535**	**0.4068**	**0.9267**	**0.0007**	**0.0494**	**0.0090**	**0.0015**	**0.0058**	**0.0067**	**0.0003**
12D	sim.	0.0032	0.3931	0.0033	0.0094	0.0143	0.0123	0.1539	0.4106	0.9296	0.0006	0.0478	0.0086	0.0015	0.0062	0.0055	0.0001
13A	**exp.**	**0.0172**	**0.4694**	**0.0010**	**0.0091**	**0.0268**	**0.0171**	**0.2923**	**0.1670**	**0.9575**	**0.0007**	**0.0114**	**0.0055**	**0.0028**	**0.0059**	**0.0159**	**0.0003**
13A	sim.	0.0196	0.4714	0.0006	0.0083	0.0263	0.0166	0.2938	0.1634	0.9571	0.0011	0.0118	0.0059	0.0034	0.0061	0.0147	0.0000
13B	**exp.**	**0.0074**	**0.6034**	**0.0004**	**0.0046**	**0.0132**	**0.0078**	**0.1508**	**0.2123**	**0.9634**	**0.0005**	**0.0122**	**0.0058**	**0.0023**	**0.0054**	**0.0081**	**0.0022**
13B	sim.	0.0031	0.6031	0.0003	0.0043	0.0133	0.0074	0.1512	0.2172	0.9635	0.0009	0.0124	0.0061	0.0024	0.0056	0.0092	0.0000
13C	**exp.**	**0.0055**	**0.6287**	**0.0003**	**0.0037**	**0.0107**	**0.0060**	**0.1205**	**0.2244**	**0.9653**	**0.0006**	**0.0124**	**0.0055**	**0.0019**	**0.0049**	**0.0064**	**0.0031**
13C	sim.	0.0018	0.6313	0.0003	0.0035	0.0107	0.0058	0.1205	0.2262	0.9656	0.0008	0.0126	0.0059	0.0021	0.0052	0.0077	0.0000
13D	**exp.**	**0.0039**	**0.6578**	**0.0003**	**0.0030**	**0.0076**	**0.0047**	**0.0843**	**0.2383**	**0.9703**	**0.0005**	**0.0122**	**0.0054**	**0.0016**	**0.0046**	**0.0048**	**0.0006**
13D	sim.	0.0008	0.6600	0.0002	0.0026	0.0076	0.0044	0.0858	0.2386	0.9686	0.0008	0.0127	0.0056	0.0016	0.0048	0.0058	0.0000

Table C1 (cont.)

ID	sim.	x'_1	x'_2	x'_3	x'_4	x'_5	x'_6	x'_7	x'_8	x''_1	x''_2	x''_3	x''_4	x''_5	x''_6	x''_7	x''_8
14A	**exp.**	**0.0422**	**0.2373**	**0.0018**	**0.0144**	**0.0351**	**0.0229**	**0.4253**	**0.2209**	**0.9559**	**0.0009**	**0.0122**	**0.0056**	**0.0032**	**0.0054**	**0.0163**	**0.0006**
14A	sim.	0.0457	0.2299	0.0021	0.0139	0.0354	0.0227	0.4295	0.2207	0.9567	0.0007	0.0120	0.0058	0.0030	0.0053	0.0165	0.0000
14B	**exp.**	**0.0203**	**0.3283**	**0.0013**	**0.0090**	**0.0212**	**0.0148**	**0.2519**	**0.3532**	**0.9680**	**0.0006**	**0.0119**	**0.0054**	**0.0019**	**0.0048**	**0.0068**	**0.0006**
14B	sim.	0.0105	0.3309	0.0011	0.0087	0.0217	0.0143	0.2551	0.3576	0.9675	0.0005	0.0121	0.0054	0.0019	0.0049	0.0076	0.0001
14C	**exp.**	**0.0120**	**0.3522**	**0.0015**	**0.0077**	**0.0185**	**0.0123**	**0.2114**	**0.3843**	**0.9705**	**0.0004**	**0.0121**	**0.0050**	**0.0016**	**0.0045**	**0.0053**	**0.0006**
14C	sim.	0.0065	0.3576	0.0009	0.0074	0.0183	0.0117	0.2106	0.3869	0.9701	0.0005	0.0121	0.0053	0.0016	0.0046	0.0058	0.0001
14D	**exp.**	**0.0108**	**0.3815**	**0.0015**	**0.0061**	**0.0142**	**0.0095**	**0.1545**	**0.4219**	**0.9751**	**0.0004**	**0.0112**	**0.0043**	**0.0012**	**0.0037**	**0.0036**	**0.0005**
14D	sim.	0.0032	0.3867	0.0008	0.0056	0.0140	0.0088	0.1553	0.4256	0.9736	0.0004	0.0120	0.0047	0.0013	0.0040	0.0038	0.0001
15A	**exp.**	**0.0459**	**0.0000**	**0.0050**	**0.0176**	**0.0392**	**0.0246**	**0.4367**	**0.4310**	**0.9652**	**0.0000**	**0.0124**	**0.0050**	**0.0021**	**0.0047**	**0.0101**	**0.0005**
15A	sim.	0.0495	0.0000	0.0051	0.0157	0.0383	0.0238	0.4401	0.4274	0.9650	0.0000	0.0119	0.0052	0.0021	0.0046	0.0110	0.0001
15B	**exp.**	**0.0376**	**0.0000**	**0.0050**	**0.0152**	**0.0327**	**0.0228**	**0.3690**	**0.5177**	**0.9710**	**0.0000**	**0.0111**	**0.0049**	**0.0016**	**0.0042**	**0.0066**	**0.0006**
15B	sim.	0.0332	0.0000	0.0041	0.0144	0.0327	0.0216	0.3698	0.5243	0.9702	0.0000	0.0113	0.0051	0.0016	0.0043	0.0075	0.0001
15C	**exp.**	**0.0330**	**0.0000**	**0.0049**	**0.0137**	**0.0290**	**0.0198**	**0.3225**	**0.5771**	**0.9738**	**0.0000**	**0.0108**	**0.0045**	**0.0014**	**0.0039**	**0.0053**	**0.0004**
15C	sim.	0.0247	0.0000	0.0036	0.0128	0.0297	0.0194	0.3216	0.5881	0.9729	0.0000	0.0113	0.0047	0.0014	0.0040	0.0056	0.0001
15D	**exp.**	**0.0280**	**0.0000**	**0.0048**	**0.0111**	**0.0223**	**0.0158**	**0.2436**	**0.6743**	**0.9767**	**0.0000**	**0.0107**	**0.0039**	**0.0010**	**0.0030**	**0.0041**	**0.0007**
15D	sim.	0.0145	0.0000	0.0032	0.0105	0.0225	0.0150	0.2450	0.6893	0.9765	0.0000	0.0115	0.0042	0.0010	0.0033	0.0034	0.0001
16A	**exp.**	**0.0492**	**0.0000**	**0.0051**	**0.0183**	**0.0335**	**0.0247**	**0.3634**	**0.5058**	**0.9594**	**0.0000**	**0.0184**	**0.0067**	**0.0017**	**0.0050**	**0.0081**	**0.0006**
16A	sim.	0.0341	0.0000	0.0063	0.0187	0.0337	0.0243	0.3698	0.5131	0.9612	0.0000	0.0174	0.0065	0.0018	0.0049	0.0081	0.0001
16B	**exp.**	**0.0364**	**0.0000**	**0.0048**	**0.0153**	**0.0305**	**0.0219**	**0.3141**	**0.5770**	**0.9632**	**0.0000**	**0.0179**	**0.0059**	**0.0017**	**0.0046**	**0.0058**	**0.0009**
16B	sim.	0.0252	0.0000	0.0056	0.0153	0.0310	0.0217	0.3212	0.5802	0.9651	0.0000	0.0172	0.0056	0.0015	0.0045	0.0060	0.0001
16C	**exp.**	**0.0294**	**0.0000**	**0.0053**	**0.0127**	**0.0237**	**0.0192**	**0.2463**	**0.6634**	**0.9676**	**0.0000**	**0.0171**	**0.0055**	**0.0011**	**0.0039**	**0.0041**	**0.0007**
16C	sim.	0.0155	0.0000	0.0048	0.0129	0.0243	0.0185	0.2500	0.6741	0.9688	0.0000	0.0170	0.0051	0.0011	0.0041	0.0038	0.0001
16D	**exp.**	**0.0627**	**0.0000**	**0.0049**	**0.0200**	**0.0377**	**0.0265**	**0.4379**	**0.4102**	**0.9526**	**0.0000**	**0.0189**	**0.0063**	**0.0026**	**0.0056**	**0.0134**	**0.0006**
16D	sim.	0.0516	0.0000	0.0075	0.0197	0.0393	0.0276	0.4413	0.4130	0.9562	0.0000	0.0176	0.0065	0.0023	0.0053	0.0121	0.0001
17A	**exp.**	**0.0018**	**0.7012**	**0.0002**	**0.0029**	**0.0070**	**0.0044**	**0.0753**	**0.2072**	**0.9559**	**0.0007**	**0.0199**	**0.0081**	**0.0019**	**0.0063**	**0.0073**	**0.0001**
17A	sim.	0.0006	0.6988	0.0003	0.0029	0.0069	0.0045	0.0770	0.2089	0.9565	0.0008	0.0198	0.0078	0.0019	0.0061	0.0071	0.0000
17B	**exp.**	**0.0008**	**0.7714**	**0.0001**	**0.0019**	**0.0050**	**0.0032**	**0.0574**	**0.1602**	**0.9537**	**0.0009**	**0.0204**	**0.0094**	**0.0017**	**0.0070**	**0.0069**	**0.0000**
17B	sim.	0.0003	0.7701	0.0002	0.0020	0.0051	0.0032	0.0564	0.1626	0.9541	0.0009	0.0196	0.0087	0.0020	0.0064	0.0083	0.0000
17C	**exp.**	**0.0023**	**0.6681**	**0.0003**	**0.0037**	**0.0100**	**0.0062**	**0.1126**	**0.1967**	**0.9511**	**0.0010**	**0.0208**	**0.0086**	**0.0023**	**0.0070**	**0.0092**	**0.0001**
17C	sim.	0.0014	0.6680	0.0004	0.0039	0.0098	0.0063	0.1094	0.2009	0.9523	0.0009	0.0199	0.0084	0.0024	0.0070	0.0092	0.0000
17D	**exp.**	**0.0012**	**0.7608**	**0.0002**	**0.0024**	**0.0066**	**0.0040**	**0.0796**	**0.1452**	**0.9451**	**0.0012**	**0.0208**	**0.0104**	**0.0026**	**0.0080**	**0.0118**	**0.0000**
17D	sim.	0.0006	0.7596	0.0002	0.0025	0.0068	0.0041	0.0766	0.1497	0.9481	0.0010	0.0200	0.0098	0.0026	0.0074	0.0111	0.0000
18A	**exp.**	**0.0097**	**0.5565**	**0.0006**	**0.0099**	**0.0334**	**0.0221**	**0.1695**	**0.1982**	**0.9388**	**0.0015**	**0.0136**	**0.0113**	**0.0062**	**0.0145**	**0.0140**	**0.0000**
18A	sim.	0.0065	0.5539	0.0004	0.0098	0.0330	0.0239	0.1744	0.1981	0.9437	0.0010	0.0138	0.0113	0.0057	0.0141	0.0104	0.0000
18B	**exp.**	**0.0071**	**0.5624**	**0.0007**	**0.0148**	**0.0092**	**0.0055**	**0.2083**	**0.1919**	**0.9393**	**0.0013**	**0.0151**	**0.0169**	**0.0017**	**0.0033**	**0.0223**	**0.0000**
18B	sim.	0.0073	0.5513	0.0005	0.0134	0.0089	0.0055	0.2184	0.1947	0.9514	0.0010	0.0145	0.0159	0.0014	0.0032	0.0126	0.0000

Table C2: Simulated and experimental equilibrium molar fractions of the extract phase, x^{I}_{i} and raffinate phase, x^{II}_{i}, for the system Hexane(1) + Water(2) + Pseudocumene(3) + Undecane(4) +Indene(5) + o-Tolunitrile(6) + o-Toluidine(7) + m-Cresol (8) +Triethylene Glycol(9)

ID		x^{I}_{1}	x^{I}_{2}	x^{I}_{3}	x^{I}_{4}	x^{I}_{5}	x^{I}_{6}	x^{I}_{7}	x^{I}_{8}	x^{I}_{9}	x^{II}_{1}	x^{II}_{2}	x^{II}_{3}	x^{II}_{4}	x^{II}_{5}	x^{II}_{6}	x^{II}_{7}	x^{II}_{8}	x^{II}_{9}
c1a	**exp.**	**0.0139**	**0.6931**	**0.0008**	**0.0000**	**0.0053**	**0.0065**	**0.0118**	**0.1477**	**0.1209**	**0.8820**	**0.0025**	**0.0146**	**0.0113**	**0.0450**	**0.0110**	**0.0077**	**0.0228**	**0.0032**
c1a	sim	0.0297	0.6709	0.0009	0.0000	0.0061	0.0068	0.0119	0.1546	0.1193	0.8959	0.0015	0.0143	0.0111	0.0443	0.0108	0.0077	0.0143	0.0000
c1b	**exp.**	**0.0061**	**0.7638**	**0.0005**	**0.0000**	**0.0024**	**0.0028**	**0.0069**	**0.0847**	**0.1328**	**0.8936**	**0.0014**	**0.0142**	**0.0119**	**0.0428**	**0.0091**	**0.0074**	**0.0165**	**0.0030**
c1b	sim	0.0038	0.7678	0.0002	0.0000	0.0021	0.0024	0.0065	0.0852	0.1320	0.8986	0.0014	0.0142	0.0116	0.0417	0.0092	0.0078	0.0153	0.0000
c1c	**exp.**	**0.0037**	**0.7897**	**0.0001**	**0.0000**	**0.0016**	**0.0024**	**0.0051**	**0.0632**	**0.1341**	**0.8874**	**0.0013**	**0.0141**	**0.0115**	**0.0426**	**0.0107**	**0.0074**	**0.0153**	**0.0097**
c1c	sim	0.0015	0.7888	0.0001	0.0000	0.0014	0.0023	0.0052	0.0625	0.1382	0.9029	0.0013	0.0141	0.0111	0.0416	0.0108	0.0070	0.0112	0.0000
c1d	**exp.**	**0.0030**	**0.7914**	**0.0003**	**0.0000**	**0.0012**	**0.0020**	**0.0044**	**0.0498**	**0.1478**	**0.9016**	**0.0010**	**0.0146**	**0.0115**	**0.0440**	**0.0106**	**0.0058**	**0.0085**	**0.0025**
c1d	sim	0.0008	0.7959	0.0001	0.0000	0.0012	0.0020	0.0043	0.0493	0.1464	0.9075	0.0012	0.0143	0.0111	0.0419	0.0102	0.0057	0.0079	0.0000
c1e	**exp.**	**0.0030**	**0.8055**	**0.0002**	**0.0000**	**0.0011**	**0.0015**	**0.0044**	**0.0351**	**0.1491**	**0.8983**	**0.0009**	**0.0155**	**0.0117**	**0.0438**	**0.0111**	**0.0068**	**0.0053**	**0.0066**
c1e	sim	0.0003	0.8104	0.0001	0.0000	0.0009	0.0017	0.0044	0.0351	0.1470	0.9086	0.0011	0.0149	0.0112	0.0418	0.0102	0.0064	0.0058	0.0000
c2a	**exp.**	**0.0234**	**0.5145**	**0.0016**	**0.0002**	**0.0103**	**0.0126**	**0.0194**	**0.2335**	**0.1846**	**0.8996**	**0.0015**	**0.0135**	**0.0109**	**0.0397**	**0.0100**	**0.0071**	**0.0166**	**0.0010**
c2a	sim	0.0843	0.4641	0.0023	0.0002	0.0128	0.0147	0.0214	0.2295	0.1708	0.9112	0.0012	0.0140	0.0118	0.0405	0.0086	0.0057	0.0071	0.0000
c2b	**exp.**	**0.0168**	**0.5825**	**0.0013**	**0.0000**	**0.0054**	**0.0095**	**0.0135**	**0.1586**	**0.2122**	**0.8967**	**0.0012**	**0.0195**	**0.0141**	**0.0379**	**0.0115**	**0.0068**	**0.0105**	**0.0017**
c2b	sim	0.0264	0.5785	0.0015	0.0001	0.0065	0.0102	0.0146	0.1602	0.2021	0.9023	0.0011	0.0190	0.0142	0.0376	0.0112	0.0058	0.0087	0.0001
c2c	**exp.**	**0.0058**	**0.6389**	**0.0005**	**0.0000**	**0.0054**	**0.0054**	**0.0099**	**0.1049**	**0.2292**	**0.9114**	**0.0015**	**0.0143**	**0.0114**	**0.0396**	**0.0088**	**0.0051**	**0.0068**	**0.0011**
c2c	sim	0.0073	0.6349	0.0006	0.0000	0.0047	0.0053	0.0101	0.1068	0.2301	0.9121	0.0010	0.0143	0.0115	0.0406	0.0090	0.0049	0.0065	0.0001
c2d	**exp.**	**0.0070**	**0.6475**	**0.0004**	**0.0000**	**0.0034**	**0.0044**	**0.0082**	**0.0819**	**0.2473**	**0.9134**	**0.0006**	**0.0141**	**0.0116**	**0.0396**	**0.0091**	**0.0045**	**0.0049**	**0.0021**
c2d	sim	0.0035	0.6454	0.0005	0.0000	0.0039	0.0045	0.0083	0.0827	0.2511	0.9166	0.0009	0.0139	0.0113	0.0392	0.0090	0.0042	0.0050	0.0001
c2e	**exp.**	**0.0052**	**0.6780**	**0.0000**	**0.0000**	**0.0028**	**0.0065**	**0.0062**	**0.0563**	**0.2451**	**0.9202**	**0.0007**	**0.0000**	**0.0117**	**0.0425**	**0.0170**	**0.0042**	**0.0029**	**0.0008**
c2e	sim	0.0015	0.6751	0.0000	0.0000	0.0034	0.0064	0.0063	0.0581	0.2492	0.9224	0.0010	0.0000	0.0115	0.0400	0.0167	0.0040	0.0044	0.0001
c3a	**exp.**	**0.0120**	**0.6120**	**0.0007**	**0.0000**	**0.0060**	**0.0072**	**0.0131**	**0.1428**	**0.2063**	**0.9055**	**0.0009**	**0.0140**	**0.0115**	**0.0408**	**0.0095**	**0.0057**	**0.0098**	**0.0024**
c3a	sim	0.0196	0.5970	0.0010	0.0000	0.0065	0.0074	0.0133	0.1458	0.2094	0.9114	0.0011	0.0139	0.0114	0.0401	0.0091	0.0054	0.0076	0.0001
c3b	**exp.**	**0.0046**	**0.7498**	**0.0003**	**0.0000**	**0.0022**	**0.0032**	**0.0065**	**0.0718**	**0.1616**	**0.9036**	**0.0013**	**0.0142**	**0.0117**	**0.0423**	**0.0095**	**0.0059**	**0.0095**	**0.0019**
c3b	sim	0.0025	0.7481	0.0002	0.0000	0.0022	0.0029	0.0064	0.0734	0.1644	0.9069	0.0012	0.0143	0.0111	0.0411	0.0100	0.0061	0.0093	0.0000
c4a	**exp.**	**0.0053**	**0.7578**	**0.0003**	**0.0000**	**0.0023**	**0.0032**	**0.0071**	**0.0894**	**0.1346**	**0.9188**	**0.0014**	**0.0109**	**0.0086**	**0.0330**	**0.0086**	**0.0058**	**0.0116**	**0.0014**
c4a	sim	0.0042	0.7600	0.0002	0.0000	0.0018	0.0027	0.0061	0.0879	0.1371	0.9182	0.0013	0.0109	0.0085	0.0326	0.0089	0.0065	0.0131	0.0000
c4b	**exp.**	**0.0141**	**0.6963**	**0.0007**	**0.0000**	**0.0046**	**0.0058**	**0.0112**	**0.1478**	**0.1194**	**0.9103**	**0.0022**	**0.0110**	**0.0087**	**0.0330**	**0.0086**	**0.0066**	**0.0183**	**0.0014**
c4b	sim	0.0277	0.6810	0.0006	0.0000	0.0043	0.0054	0.0106	0.1519	0.1185	0.9175	0.0014	0.0109	0.0087	0.0328	0.0086	0.0067	0.0134	0.0000
c4c	**exp.**	**0.0040**	**0.7792**	**0.0001**	**0.0000**	**0.0015**	**0.0022**	**0.0050**	**0.0645**	**0.1435**	**0.9226**	**0.0012**	**0.0110**	**0.0087**	**0.0332**	**0.0085**	**0.0054**	**0.0073**	**0.0021**
c4c	sim	0.0015	0.7834	0.0001	0.0000	0.0012	0.0020	0.0048	0.0629	0.1441	0.9238	0.0011	0.0108	0.0085	0.0324	0.0085	0.0055	0.0093	0.0000
c4d	**exp.**	**0.0033**	**0.7933**	**0.0001**	**0.0000**	**0.0011**	**0.0017**	**0.0041**	**0.0482**	**0.1482**	**0.9234**	**0.0010**	**0.0115**	**0.0086**	**0.0337**	**0.0085**	**0.0051**	**0.0072**	**0.0010**
c4d	sim	0.0008	0.7936	0.0001	0.0000	0.0010	0.0017	0.0041	0.0488	0.1498	0.9258	0.0011	0.0114	0.0085	0.0331	0.0082	0.0050	0.0069	0.0000
c4e	**exp.**	**0.0038**	**0.8076**	**0.0001**	**0.0000**	**0.0007**	**0.0012**	**0.0031**	**0.0331**	**0.1504**	**0.9242**	**0.0010**	**0.0115**	**0.0086**	**0.0350**	**0.0085**	**0.0047**	**0.0059**	**0.0007**
c4e	sim	0.0003	0.8130	0.0001	0.0000	0.0008	0.0013	0.0032	0.0344	0.1469	0.9278	0.0010	0.0111	0.0086	0.0342	0.0080	0.0043	0.0050	0.0000
c5a	**exp.**	**0.0299**	**0.5330**	**0.0011**	**0.0001**	**0.0093**	**0.0105**	**0.0183**	**0.2226**	**0.1752**	**0.9185**	**0.0013**	**0.0110**	**0.0087**	**0.0315**	**0.0078**	**0.0060**	**0.0134**	**0.0019**
c5a	sim	0.0811	0.4849	0.0017	0.0001	0.0096	0.0115	0.0189	0.2255	0.1667	0.9295	0.0011	0.0107	0.0087	0.0311	0.0069	0.0051	0.0069	0.0000

Table C2 cont.

ID	sim.	x'_1	x'_2	x'_3	x'_4	x'_5	x'_6	x'_7	x'_8	x'_9	x''_1	x''_2	x''_3	x''_4	x''_5	x''_6	x''_7	x''_8	x''_9
c5b	**exp.**	**0.0131**	**0.5995**	**0.0006**	**0.0000**	**0.0047**	**0.0065**	**0.0126**	**0.1450**	**0.2180**	**0.9274**	**0.0009**	**0.0107**	**0.0085**	**0.0308**	**0.0075**	**0.0049**	**0.0082**	**0.0011**
c5b	sim	0.0195	0.5896	0.0008	0.0000	0.0054	0.0066	0.0129	0.1471	0.2180	0.9288	0.0010	0.0107	0.0088	0.0314	0.0075	0.0048	0.0069	0.0000
c5c	**exp.**	**0.0076**	**0.6279**	**0.0004**	**0.0000**	**0.0034**	**0.0046**	**0.0090**	**0.1050**	**0.2421**	**0.9287**	**0.0007**	**0.0113**	**0.0087**	**0.0315**	**0.0076**	**0.0047**	**0.0067**	**0.0001**
c5c	sim	0.0071	0.6340	0.0005	0.0000	0.0038	0.0046	0.0095	0.1063	0.2342	0.9307	0.0009	0.0108	0.0086	0.0313	0.0075	0.0043	0.0059	0.0001
c5d	**exp.**	**0.0043**	**0.6603**	**0.0002**	**0.0000**	**0.0028**	**0.0037**	**0.0079**	**0.0831**	**0.2376**	**0.9273**	**0.0008**	**0.0117**	**0.0092**	**0.0331**	**0.0078**	**0.0041**	**0.0049**	**0.0011**
c5d	sim	0.0035	0.6581	0.0004	0.0000	0.0030	0.0036	0.0079	0.0831	0.2404	0.9331	0.0009	0.0107	0.0085	0.0305	0.0073	0.0039	0.0050	0.0001
c5e	**exp.**	**0.0016**	**0.6852**	**0.0002**	**0.0000**	**0.0021**	**0.0030**	**0.0060**	**0.0590**	**0.2429**	**0.9320**	**0.0006**	**0.0116**	**0.0091**	**0.0333**	**0.0069**	**0.0032**	**0.0029**	**0.0005**
c5e	sim	0.0014	0.6833	0.0003	0.0000	0.0023	0.0027	0.0058	0.0586	0.2456	0.9355	0.0008	0.0108	0.0085	0.0305	0.0070	0.0032	0.0037	0.0001
c6b	**exp.**	**0.0330**	**0.3191**	**0.0021**	**0.0002**	**0.0161**	**0.0137**	**0.0228**	**0.2404**	**0.3526**	**0.9041**	**0.0007**	**0.0144**	**0.0113**	**0.0490**	**0.0085**	**0.0047**	**0.0066**	**0.0005**
c6b	sim	0.0628	0.3056	0.0025	0.0002	0.0191	0.0153	0.0230	0.2394	0.3321	0.9112	0.0007	0.0140	0.0115	0.0466	0.0073	0.0044	0.0042	0.0001
c6c	**exp.**	**0.0186**	**0.3641**	**0.0000**	**0.0002**	**0.0129**	**0.0114**	**0.0194**	**0.1855**	**0.3878**	**0.9228**	**0.0005**	**0.0000**	**0.0222**	**0.0380**	**0.0076**	**0.0036**	**0.0047**	**0.0006**
c6c	sim	0.0268	0.3572	0.0000	0.0004	0.0113	0.0116	0.0189	0.1841	0.3896	0.9244	0.0006	0.0000	0.0222	0.0375	0.0072	0.0037	0.0042	0.0001
c6d	**exp.**	**0.0130**	**0.4077**	**0.0000**	**0.0001**	**0.0093**	**0.0087**	**0.0158**	**0.1411**	**0.4045**	**0.9219**	**0.0005**	**0.0000**	**0.0231**	**0.0398**	**0.0074**	**0.0033**	**0.0035**	**0.0004**
c6d	sim	0.0133	0.4125	0.0000	0.0003	0.0094	0.0092	0.0158	0.1424	0.3971	0.9220	0.0006	0.0000	0.0228	0.0398	0.0074	0.0035	0.0038	0.0001
c6e	**exp.**	**0.0093**	**0.4212**	**0.0000**	**0.0002**	**0.0097**	**0.0075**	**0.0119**	**0.1059**	**0.4343**	**0.9272**	**0.0004**	**0.0000**	**0.0227**	**0.0363**	**0.0068**	**0.0025**	**0.0034**	**0.0007**
c6e	sim	0.0062	0.4174	0.0000	0.0003	0.0077	0.0072	0.0118	0.1073	0.4421	0.9269	0.0005	0.0000	0.0228	0.0376	0.0067	0.0026	0.0027	0.0001
c7a	**exp.**	**0.0400**	**0.5258**	**0.0008**	**0.0001**	**0.0071**	**0.0095**	**0.0156**	**0.2277**	**0.1735**	**0.9319**	**0.0014**	**0.0088**	**0.0070**	**0.0262**	**0.0062**	**0.0054**	**0.0126**	**0.0005**
c7a	sim	0.0813	0.4875	0.0014	0.0001	0.0080	0.0101	0.0174	0.2264	0.1679	0.9400	0.0010	0.0088	0.0071	0.0258	0.0060	0.0046	0.0066	0.0000
c7b	**exp.**	**0.0171**	**0.5898**	**0.0004**	**0.0000**	**0.0042**	**0.0057**	**0.0117**	**0.1503**	**0.2207**	**0.9391**	**0.0008**	**0.0087**	**0.0070**	**0.0265**	**0.0065**	**0.0042**	**0.0071**	**0.0001**
c7b	sim	0.0189	0.5937	0.0006	0.0000	0.0045	0.0057	0.0116	0.1459	0.2191	0.9400	0.0009	0.0087	0.0070	0.0261	0.0065	0.0043	0.0065	0.0000
c7c	**exp.**	**0.0100**	**0.6290**	**0.0004**	**0.0000**	**0.0034**	**0.0041**	**0.0096**	**0.1072**	**0.2362**	**0.9366**	**0.0006**	**0.0092**	**0.0070**	**0.0302**	**0.0065**	**0.0041**	**0.0058**	**0.0001**
c7c	sim	0.0069	0.6354	0.0004	0.0000	0.0036	0.0039	0.0093	0.1053	0.2351	0.9383	0.0009	0.0088	0.0069	0.0290	0.0063	0.0041	0.0056	0.0001
c7d	**exp.**	**0.0076**	**0.6574**	**0.0003**	**0.0000**	**0.0023**	**0.0035**	**0.0075**	**0.0827**	**0.2388**	**0.9419**	**0.0006**	**0.0091**	**0.0072**	**0.0264**	**0.0064**	**0.0036**	**0.0046**	**0.0004**
c7d	sim	0.0034	0.6615	0.0003	0.0000	0.0025	0.0032	0.0073	0.0822	0.2396	0.9431	0.0008	0.0087	0.0069	0.0257	0.0064	0.0036	0.0048	0.0001
c7e	**exp.**	**0.0035**	**0.6909**	**0.0002**	**0.0000**	**0.0018**	**0.0024**	**0.0052**	**0.0570**	**0.2389**	**0.9438**	**0.0005**	**0.0089**	**0.0071**	**0.0262**	**0.0064**	**0.0031**	**0.0038**	**0.0002**
c7e	sim	0.0013	0.6940	0.0002	0.0000	0.0019	0.0024	0.0052	0.0563	0.2387	0.9455	0.0008	0.0086	0.0068	0.0253	0.0063	0.0030	0.0036	0.0001
c8a	**exp.**	**0.0227**	**0.6828**	**0.0004**	**0.0000**	**0.0036**	**0.0051**	**0.0103**	**0.1538**	**0.1213**	**0.9281**	**0.0009**	**0.0090**	**0.0069**	**0.0267**	**0.0073**	**0.0060**	**0.0145**	**0.0006**
c8a	sim	0.0285	0.6756	0.0005	0.0000	0.0037	0.0049	0.0102	0.1539	0.1226	0.9313	0.0012	0.0089	0.0069	0.0266	0.0072	0.0058	0.0119	0.0000
c8b	**exp.**	**0.0085**	**0.7592**	**0.0001**	**0.0000**	**0.0016**	**0.0028**	**0.0061**	**0.0885**	**0.1332**	**0.9297**	**0.0013**	**0.0087**	**0.0069**	**0.0303**	**0.0070**	**0.0054**	**0.0100**	**0.0007**
c8b	sim	0.0039	0.7636	0.0002	0.0000	0.0016	0.0022	0.0057	0.0859	0.1369	0.9280	0.0012	0.0088	0.0069	0.0303	0.0074	0.0057	0.0117	0.0000
c8c	**exp.**	**0.0044**	**0.7853**	**0.0001**	**0.0000**	**0.0011**	**0.0020**	**0.0045**	**0.0631**	**0.1395**	**0.9316**	**0.0049**	**0.0090**	**0.0069**	**0.0267**	**0.0073**	**0.0049**	**0.0086**	**0.0001**
c8c	sim	0.0014	0.7913	0.0001	0.0000	0.0009	0.0017	0.0043	0.0607	0.1396	0.9355	0.0011	0.0088	0.0068	0.0265	0.0073	0.0051	0.0089	0.0000
c8d	**exp.**	**0.0021**	**0.7986**	**0.0001**	**0.0000**	**0.0009**	**0.0015**	**0.0040**	**0.0485**	**0.1443**	**0.9332**	**0.0053**	**0.0090**	**0.0070**	**0.0269**	**0.0072**	**0.0045**	**0.0068**	**0.0001**
c8d	sim	0.0007	0.8029	0.0001	0.0000	0.0008	0.0014	0.0038	0.0478	0.1425	0.9373	0.0010	0.0089	0.0071	0.0267	0.0072	0.0048	0.0070	0.0000
c8e	**exp.**	**0.0015**	**0.8137**	**0.0001**	**0.0000**	**0.0007**	**0.0011**	**0.0028**	**0.0333**	**0.1468**	**0.9345**	**0.0049**	**0.0089**	**0.0070**	**0.0275**	**0.0071**	**0.0041**	**0.0058**	**0.0004**
c8e	sim	0.0003	0.8144	0.0001	0.0000	0.0006	0.0012	0.0029	0.0340	0.1466	0.9412	0.0010	0.0089	0.0069	0.0269	0.0067	0.0037	0.0047	0.0000

Table C2 (cont.)

ID	sim.	x'_1	x'_2	x'_3	x'_4	x'_5	x'_6	x'_7	x'_8	x'_9	x''_1	x''_2	x''_3	x''_4	x''_5	x''_6	x''_7	x''_8	x''_9
c9a	exp.	0.0757	0.2242	0.0128	0.0029	0.0600	0.0309	0.0375	0.3209	0.2349	0.7182	0.0031	0.0509	0.0552	0.1193	0.0174	0.0112	0.0241	0.0005
c9a	sim	0.1473	0.2032	0.0100	0.0023	0.0561	0.0301	0.0358	0.3035	0.2116	0.6855	0.0017	0.0663	0.0672	0.1420	0.0156	0.0083	0.0129	0.0005
c9b	exp.	0.0321	0.2998	0.0083	0.0010	0.0402	0.0224	0.0280	0.2332	0.3351	0.7352	0.0014	0.0527	0.0546	0.1201	0.0167	0.0081	0.0109	0.0003
c9b	sim	0.0614	0.2935	0.0068	0.0009	0.0393	0.0226	0.0279	0.2316	0.3162	0.7075	0.0014	0.0627	0.0610	0.1350	0.0161	0.0074	0.0084	0.0005
c9c	exp.	0.0290	0.3478	0.0061	0.0006	0.0325	0.0177	0.0216	0.1786	0.3661	0.7202	0.0011	0.0595	0.0648	0.1231	0.0162	0.0066	0.0084	0.0001
c9c	sim	0.0291	0.3437	0.0047	0.0006	0.0295	0.0174	0.0216	0.1822	0.3712	0.7114	0.0012	0.0629	0.0621	0.1331	0.0158	0.0061	0.0067	0.0006
c9d	exp.	0.0181	0.3764	0.0048	0.0005	0.0274	0.0143	0.0184	0.1434	0.3967	0.7371	0.0009	0.0583	0.0597	0.1159	0.0140	0.0054	0.0063	0.0023
c9d	sim	0.0159	0.3762	0.0037	0.0005	0.0240	0.0140	0.0183	0.1473	0.4001	0.7292	0.0011	0.0599	0.0564	0.1275	0.0148	0.0054	0.0052	0.0005
c9e	exp.	0.0139	0.4000	0.0038	0.0004	0.0218	0.0110	0.0130	0.1065	0.4295	0.7547	0.0007	0.0573	0.0623	0.1051	0.0121	0.0036	0.0039	0.0002
c9e	sim	0.0067	0.4057	0.0026	0.0005	0.0180	0.0105	0.0131	0.1069	0.4360	0.7365	0.0010	0.0595	0.0585	0.1224	0.0137	0.0040	0.0039	0.0005
c10a	exp.	0.0923	0.2485	0.0020	0.0001	0.0125	0.0162	0.0271	0.3386	0.2627	0.9341	0.0008	0.0088	0.0069	0.0264	0.0062	0.0050	0.0117	0.0001
c10a	sim	0.1570	0.2200	0.0023	0.0004	0.0155	0.0176	0.0271	0.3245	0.2356	0.9415	0.0006	0.0090	0.0072	0.0264	0.0055	0.0043	0.0054	0.0001
c10b	exp.	0.0285	0.3301	0.0013	0.0001	0.0096	0.0115	0.0210	0.2441	0.3537	0.9412	0.0004	0.0089	0.0072	0.0261	0.0059	0.0039	0.0064	0.0001
c10b	sim	0.0596	0.3135	0.0015	0.0002	0.0103	0.0123	0.0207	0.2404	0.3415	0.9449	0.0006	0.0089	0.0071	0.0252	0.0056	0.0037	0.0040	0.0001
c10c	exp.	0.0199	0.3675	0.0010	0.0001	0.0078	0.0089	0.0172	0.1823	0.3952	0.9459	0.0004	0.0090	0.0071	0.0251	0.0055	0.0033	0.0036	0.0001
c10c	sim	0.0268	0.3581	0.0011	0.0001	0.0079	0.0093	0.0171	0.1854	0.3941	0.9471	0.0005	0.0086	0.0069	0.0249	0.0053	0.0032	0.0032	0.0001
c10d	exp.	0.0169	0.3891	0.0007	0.0000	0.0073	0.0079	0.0147	0.1499	0.4135	0.9485	0.0003	0.0090	0.0071	0.0247	0.0053	0.0026	0.0025	0.0001
c10d	sim	0.0144	0.3887	0.0009	0.0001	0.0066	0.0078	0.0143	0.1494	0.4177	0.9477	0.0005	0.0088	0.0069	0.0250	0.0054	0.0029	0.0027	0.0001
c10e	exp.	0.0104	0.4097	0.0008	0.0001	0.0065	0.0065	0.0112	0.1081	0.4468	0.9507	0.0003	0.0087	0.0070	0.0240	0.0051	0.0022	0.0018	0.0002
c10e	sim	0.0061	0.4131	0.0007	0.0001	0.0052	0.0061	0.0111	0.1082	0.4493	0.9509	0.0005	0.0085	0.0067	0.0238	0.0052	0.0023	0.0020	0.0001
c11a	exp.	0.1256	0.0000	0.0050	0.0009	0.0315	0.0260	0.0402	0.4419	0.3289	0.9122	0.0000	0.0132	0.0113	0.0363	0.0083	0.0059	0.0125	0.0003
c11a	sim	0.2413	0.0000	0.0055	0.0014	0.0407	0.0251	0.0375	0.3770	0.2716	0.9185	0.0000	0.0138	0.0119	0.0347	0.0078	0.0046	0.0085	0.0002
c11b	exp.	0.0598	0.0000	0.0032	0.0004	0.0261	0.0186	0.0293	0.2771	0.5855	0.9241	0.0000	0.0135	0.0131	0.0352	0.0068	0.0037	0.0035	0.0001
c11b	sim	0.0856	0.0000	0.0040	0.0008	0.0266	0.0180	0.0284	0.2678	0.5688	0.9273	0.0000	0.0130	0.0127	0.0337	0.0066	0.0033	0.0031	0.0002
c11c	exp.	0.0757	0.0000	0.0039	0.0005	0.0288	0.0237	0.0353	0.3417	0.4904	0.9222	0.0000	0.0141	0.0120	0.0373	0.0072	0.0036	0.0033	0.0002
c11c	sim	0.1341	0.0000	0.0046	0.0008	0.0319	0.0214	0.0321	0.3212	0.4539	0.9220	0.0000	0.0138	0.0119	0.0353	0.0078	0.0041	0.0049	0.0002
c11d	exp.	0.0501	0.0000	0.0033	0.0006	0.0240	0.0172	0.0254	0.2380	0.6413	0.9250	0.0000	0.0138	0.0119	0.0368	0.0067	0.0030	0.0026	0.0002
c11d	sim	0.0622	0.0000	0.0039	0.0007	0.0255	0.0168	0.0251	0.2320	0.6337	0.9299	0.0000	0.0132	0.0114	0.0341	0.0062	0.0027	0.0023	0.0002
c11e	exp.	0.0354	0.0000	0.0032	0.0005	0.0215	0.0146	0.0213	0.1787	0.7249	0.9326	0.0000	0.0133	0.0118	0.0333	0.0051	0.0020	0.0013	0.0005
c11e	sim	0.0345	0.0000	0.0035	0.0007	0.0213	0.0143	0.0215	0.1773	0.7268	0.9353	0.0000	0.0127	0.0114	0.0316	0.0052	0.0021	0.0015	0.0002
c12a	exp.	0.1127	0.0000	0.0040	0.0006	0.0246	0.0229	0.0392	0.4502	0.3459	0.9258	0.0000	0.0105	0.0086	0.0301	0.0073	0.0055	0.0118	0.0004
c12a	sim	0.2385	0.0000	0.0042	0.0010	0.0336	0.0221	0.0367	0.3834	0.2806	0.9335	0.0000	0.0107	0.0088	0.0277	0.0067	0.0044	0.0080	0.0001
c12b	exp.	0.0770	0.0000	0.0029	0.0003	0.0201	0.0193	0.0324	0.3445	0.5035	0.9352	0.0000	0.0107	0.0090	0.0297	0.0065	0.0039	0.0049	0.0000
c12b	sim	0.1340	0.0000	0.0035	0.0006	0.0263	0.0185	0.0309	0.3257	0.4606	0.9372	0.0000	0.0106	0.0089	0.0282	0.0065	0.0039	0.0046	0.0002

Table C2 (cont.)

ID	x'_1	x'_2	x'_3	x'_4	x'_5	x'_6	x'_7	x'_8	x'_9	x''_1	x''_2	x''_3	x''_4	x''_5	x''_6	x''_7	x''_8	x''_9
c12c exp.	**0.0669**	**0.0000**	**0.0024**	**0.0002**	**0.0190**	**0.0165**	**0.0274**	**0.2785**	**0.5891**	**0.9395**	**0.0000**	**0.0108**	**0.0094**	**0.0285**	**0.0057**	**0.0029**	**0.0031**	**0.0000**
c12c sim	0.0862	0.0000	0.0032	0.0006	0.0225	0.0163	0.0269	0.2718	0.5725	0.9403	0.0000	0.0105	0.0095	0.0276	0.0058	0.0031	0.0030	0.0002
c12d exp.	**0.0503**	**0.0000**	**0.0022**	**0.0002**	**0.0180**	**0.0149**	**0.0246**	**0.2371**	**0.6527**	**0.9420**	**0.0000**	**0.0106**	**0.0087**	**0.0278**	**0.0057**	**0.0027**	**0.0025**	**0.0000**
c12d sim	0.0613	0.0000	0.0030	0.0005	0.0208	0.0152	0.0243	0.2338	0.6411	0.9433	0.0000	0.0103	0.0088	0.0273	0.0054	0.0026	0.0022	0.0002
c12e exp.	**0.0561**	**0.0000**	**0.0020**	**0.0002**	**0.0188**	**0.0123**	**0.0198**	**0.1741**	**0.7167**	**0.9456**	**0.0000**	**0.0107**	**0.0089**	**0.0265**	**0.0048**	**0.0020**	**0.0015**	**0.0000**
c12e sim	0.0333	0.0000	0.0028	0.0006	0.0185	0.0128	0.0202	0.1764	0.7354	0.9463	0.0000	0.0102	0.0087	0.0268	0.0046	0.0019	0.0014	0.0002
c13a exp.	**0.1121**	**0.0000**	**0.0032**	**0.0005**	**0.0207**	**0.0220**	**0.0362**	**0.4509**	**0.3544**	**0.9352**	**0.0000**	**0.0090**	**0.0071**	**0.0260**	**0.0062**	**0.0048**	**0.0117**	**0.0000**
c13a sim	0.2338	0.0000	0.0032	0.0008	0.0289	0.0194	0.0337	0.3882	0.2919	0.9429	0.0000	0.0087	0.0071	0.0235	0.0059	0.0040	0.0077	0.0001
c13b exp.	**0.0455**	**0.0000**	**0.0034**	**0.0004**	**0.0171**	**0.0199**	**0.0332**	**0.3556**	**0.5249**	**0.9455**	**0.0000**	**0.0096**	**0.0069**	**0.0247**	**0.0051**	**0.0032**	**0.0050**	**0.0000**
c13b sim	0.1331	0.0000	0.0031	0.0005	0.0220	0.0163	0.0290	0.3287	0.4673	0.9460	0.0000	0.0097	0.0071	0.0234	0.0056	0.0036	0.0045	0.0002
c13c exp.	**0.0629**	**0.0000**	**0.0027**	**0.0005**	**0.0173**	**0.0161**	**0.0280**	**0.2842**	**0.5883**	**0.9492**	**0.0000**	**0.0086**	**0.0073**	**0.0241**	**0.0052**	**0.0027**	**0.0029**	**0.0000**
c13c sim	0.0875	0.0000	0.0026	0.0005	0.0196	0.0153	0.0262	0.2757	0.5727	0.9495	0.0000	0.0086	0.0072	0.0234	0.0054	0.0029	0.0029	0.0002
c13d exp.	**0.0667**	**0.0000**	**0.0021**	**0.0004**	**0.0177**	**0.0148**	**0.0247**	**0.2340**	**0.6396**	**0.9519**	**0.0000**	**0.0086**	**0.0069**	**0.0236**	**0.0047**	**0.0022**	**0.0020**	**0.0002**
c13d sim	0.0603	0.0000	0.0025	0.0004	0.0182	0.0141	0.0237	0.2339	0.6469	0.9513	0.0000	0.0085	0.0071	0.0235	0.0049	0.0025	0.0021	0.0002
c13e exp.	**0.0335**	**0.0000**	**0.0050**	**0.0020**	**0.0221**	**0.0116**	**0.0190**	**0.1805**	**0.7264**	**0.9591**	**0.0000**	**0.0073**	**0.0066**	**0.0191**	**0.0044**	**0.0019**	**0.0015**	**0.0001**
c13e sim	0.0337	0.0000	0.0023	0.0005	0.0155	0.0120	0.0193	0.1796	0.7373	0.9550	0.0000	0.0084	0.0070	0.0221	0.0042	0.0018	0.0014	0.0002
c14a exp.	**0.0021**	**0.6619**	**0.0010**	**0.0000**	**0.0093**	**0.0060**	**0.0085**	**0.0726**	**0.2386**	**0.6450**	**0.0056**	**0.0733**	**0.0630**	**0.1655**	**0.0249**	**0.0082**	**0.0088**	**0.0057**
c14a sim	0.0024	0.6652	0.0009	0.0001	0.0087	0.0058	0.0083	0.0699	0.2387	0.7133	0.0021	0.0597	0.0501	0.1371	0.0213	0.0076	0.0086	0.0003
c14b exp.	**0.0027**	**0.6699**	**0.0006**	**0.0000**	**0.0060**	**0.0053**	**0.0079**	**0.0696**	**0.2380**	**0.8118**	**0.0030**	**0.0363**	**0.0301**	**0.0922**	**0.0149**	**0.0056**	**0.0049**	**0.0012**
c14b sim	0.0023	0.6679	0.0007	0.0001	0.0064	0.0052	0.0078	0.0699	0.2398	0.8157	0.0014	0.0358	0.0295	0.0898	0.0154	0.0058	0.0065	0.0002
c14c exp.	**0.0023**	**0.6738**	**0.0005**	**0.0000**	**0.0039**	**0.0043**	**0.0075**	**0.0694**	**0.2383**	**0.8850**	**0.0013**	**0.0208**	**0.0170**	**0.0568**	**0.0108**	**0.0045**	**0.0037**	**0.0001**
c14c sim	0.0022	0.6727	0.0005	0.0000	0.0042	0.0042	0.0073	0.0691	0.2396	0.8873	0.0011	0.0201	0.0163	0.0545	0.0109	0.0046	0.0052	0.0001
c14d exp.	**0.0141**	**0.6666**	**0.0003**	**0.0000**	**0.0031**	**0.0036**	**0.0070**	**0.0682**	**0.2368**	**0.9086**	**0.0005**	**0.0151**	**0.0121**	**0.0428**	**0.0086**	**0.0043**	**0.0032**	**0.0047**
c14d sim	0.0022	0.6723	0.0004	0.0000	0.0033	0.0036	0.0071	0.0697	0.2414	0.9173	0.0009	0.0140	0.0112	0.0393	0.0085	0.0040	0.0046	0.0001
c14e exp.	**0.0152**	**0.6563**	**0.0003**	**0.0000**	**0.0030**	**0.0036**	**0.0068**	**0.0680**	**0.2467**	**0.9347**	**0.0004**	**0.0109**	**0.0101**	**0.0308**	**0.0068**	**0.0032**	**0.0030**	**0.0001**
c14e sim	0.0021	0.6668	0.0003	0.0000	0.0027	0.0032	0.0067	0.0684	0.2499	0.9326	0.0008	0.0108	0.0099	0.0309	0.0072	0.0035	0.0042	0.0001
c15a exp.	**0.0576**	**0.0000**	**0.0033**	**0.0008**	**0.0174**	**0.0130**	**0.0214**	**0.1970**	**0.6896**	**0.9532**	**0.0000**	**0.0087**	**0.0070**	**0.0228**	**0.0045**	**0.0019**	**0.0016**	**0.0001**
c15a sim	0.0434	0.0000	0.0025	0.0004	0.0165	0.0130	0.0211	0.2021	0.7009	0.9530	0.0000	0.0089	0.0070	0.0227	0.0045	0.0020	0.0016	0.0002
c15b exp.	**0.0472**	**0.3830**	**0.0013**	**0.0001**	**0.0079**	**0.0064**	**0.0117**	**0.1231**	**0.4192**	**0.9518**	**0.0003**	**0.0083**	**0.0069**	**0.0230**	**0.0050**	**0.0024**	**0.0021**	**0.0001**
c15b sim	0.0089	0.4014	0.0008	0.0001	0.0059	0.0067	0.0123	0.1251	0.4389	0.9490	0.0005	0.0087	0.0070	0.0247	0.0052	0.0025	0.0023	0.0001
c15c exp.	**0.0215**	**0.6610**	**0.0004**	**0.0000**	**0.0025**	**0.0030**	**0.0062**	**0.0671**	**0.2382**	**0.9455**	**0.0006**	**0.0087**	**0.0068**	**0.0253**	**0.0060**	**0.0032**	**0.0038**	**0.0001**
c15c sim	0.0021	0.6697	0.0003	0.0000	0.0022	0.0027	0.0063	0.0680	0.2487	0.9447	0.0008	0.0088	0.0069	0.0255	0.0061	0.0032	0.0039	0.0001
c15d exp.	**0.0091**	**0.8004**	**0.0001**	**0.0000**	**0.0007**	**0.0013**	**0.0032**	**0.0406**	**0.1446**	**0.9370**	**0.0005**	**0.0093**	**0.0072**	**0.0276**	**0.0074**	**0.0043**	**0.0066**	**0.0001**
c15d sim	0.0005	0.8060	0.0001	0.0000	0.0007	0.0013	0.0033	0.0404	0.1477	0.9401	0.0010	0.0088	0.0070	0.0264	0.0071	0.0041	0.0056	0.0000
c15e exp.	**0.0022**	**0.8588**	**0.0000**	**0.0000**	**0.0003**	**0.0007**	**0.0021**	**0.0282**	**0.1076**	**0.9339**	**0.0007**	**0.0093**	**0.0073**	**0.0286**	**0.0077**	**0.0050**	**0.0073**	**0.0001**
c15e sim	0.0002	0.8634	0.0000	0.0000	0.0003	0.0008	0.0022	0.0284	0.1047	0.9377	0.0011	0.0089	0.0070	0.0276	0.0071	0.0046	0.0060	0.0000

Table C2 (cont.)

ID	x'_1	x'_2	x'_3	x'_4	x'_5	x'_6	x'_7	x'_8	x'_9	x''_1	x''_2	x''_3	x''_4	x''_5	x''_6	x''_7	x''_8	x''_9
c16a exp.	**0.0271**	**0.3369**	**0.0013**	**0.0001**	**0.0102**	**0.0115**	**0.0217**	**0.2431**	**0.3482**	**0.9308**	**0.0005**	**0.0108**	**0.0087**	**0.0314**	**0.0071**	**0.0042**	**0.0063**	**0.0001**
c16a sim	0.0614	0.3111	0.0019	0.0002	0.0124	0.0136	0.0219	0.2413	0.3362	0.9348	0.0006	0.0108	0.0088	0.0305	0.0062	0.0040	0.0041	0.0001
c16b exp.	**0.0463**	**0.3563**	**0.0010**	**0.0001**	**0.0099**	**0.0096**	**0.0176**	**0.1821**	**0.3771**	**0.9358**	**0.0004**	**0.0109**	**0.0088**	**0.0304**	**0.0066**	**0.0035**	**0.0034**	**0.0001**
c16b sim	0.0270	0.3585	0.0014	0.0001	0.0094	0.0105	0.0180	0.1849	0.3902	0.9374	0.0005	0.0105	0.0086	0.0299	0.0061	0.0035	0.0033	0.0001
c16c exp.	**0.0542**	**0.2506**	**0.0023**	**0.0003**	**0.0163**	**0.0173**	**0.0292**	**0.3537**	**0.2761**	**0.9225**	**0.0010**	**0.0110**	**0.0087**	**0.0313**	**0.0075**	**0.0057**	**0.0122**	**0.0001**
c16c sim	0.1573	0.2116	0.0028	0.0005	0.0176	0.0196	0.0293	0.3244	0.2370	0.9333	0.0006	0.0108	0.0088	0.0300	0.0061	0.0047	0.0056	0.0001
c16d exp.	**0.0251**	**0.3815**	**0.0009**	**0.0001**	**0.0090**	**0.0085**	**0.0155**	**0.1451**	**0.4143**	**0.9382**	**0.0005**	**0.0111**	**0.0089**	**0.0293**	**0.0063**	**0.0030**	**0.0025**	**0.0001**
c16d sim	0.0144	0.3823	0.0011	0.0001	0.0079	0.0086	0.0154	0.1490	0.4211	0.9386	0.0005	0.0105	0.0086	0.0298	0.0059	0.0031	0.0028	0.0001
c16e exp.	**0.0377**	**0.4015**	**0.0008**	**0.0001**	**0.0070**	**0.0067**	**0.0107**	**0.1034**	**0.4320**	**0.9397**	**0.0003**	**0.0117**	**0.0091**	**0.0292**	**0.0059**	**0.0023**	**0.0016**	**0.0001**
c16e sim	0.0061	0.4138	0.0009	0.0001	0.0062	0.0066	0.0112	0.1077	0.4474	0.9409	0.0005	0.0108	0.0085	0.0289	0.0058	0.0024	0.0021	0.0001
c17b exp.	**0.0380**	**0.3573**	**0.0017**	**0.0003**	**0.0120**	**0.0113**	**0.0183**	**0.1813**	**0.3799**	**0.9183**	**0.0004**	**0.0143**	**0.0115**	**0.0390**	**0.0077**	**0.0042**	**0.0043**	**0.0001**
c17b sim	0.0278	0.3570	0.0018	0.0002	0.0117	0.0119	0.0188	0.1851	0.3857	0.9216	0.0006	0.0137	0.0114	0.0381	0.0072	0.0038	0.0035	0.0001
c17d exp.	**0.0203**	**0.4038**	**0.0015**	**0.0002**	**0.0106**	**0.0083**	**0.0134**	**0.1237**	**0.4182**	**0.9239**	**0.0003**	**0.0143**	**0.0121**	**0.0371**	**0.0070**	**0.0029**	**0.0022**	**0.0001**
c17d sim	0.0093	0.4004	0.0013	0.0002	0.0085	0.0083	0.0136	0.1256	0.4329	0.9239	0.0005	0.0139	0.0117	0.0375	0.0068	0.0030	0.0025	0.0001
c17e exp.	**0.0221**	**0.4053**	**0.0016**	**0.0002**	**0.0092**	**0.0073**	**0.0115**	**0.1083**	**0.4344**	**0.9257**	**0.0002**	**0.0138**	**0.0117**	**0.0372**	**0.0068**	**0.0026**	**0.0018**	**0.0001**
c17e sim	0.0063	0.4131	0.0011	0.0001	0.0078	0.0074	0.0117	0.1078	0.4447	0.9256	0.0005	0.0137	0.0113	0.0372	0.0067	0.0026	0.0022	0.0001
c18a exp.	**0.0289**	**0.0000**	**0.0030**	**0.0007**	**0.0191**	**0.0144**	**0.0220**	**0.2093**	**0.7025**	**0.9457**	**0.0000**	**0.0098**	**0.0087**	**0.0267**	**0.0049**	**0.0023**	**0.0019**	**0.0000**
c18a sim	0.0449	0.0000	0.0028	0.0006	0.0192	0.0140	0.0217	0.2035	0.6932	0.9530	0.0000	0.0089	0.0070	0.0227	0.0045	0.0020	0.0016	0.0002
c18b exp.	**0.0153**	**0.3992**	**0.0014**	**0.0003**	**0.0088**	**0.0078**	**0.0133**	**0.1252**	**0.4288**	**0.9426**	**0.0003**	**0.0102**	**0.0087**	**0.0280**	**0.0056**	**0.0025**	**0.0020**	**0.0002**
c18b sim	0.0093	0.4016	0.0010	0.0001	0.0071	0.0074	0.0132	0.1264	0.4338	0.9387	0.0005	0.0107	0.0088	0.0301	0.0059	0.0028	0.0024	0.0001
c18c exp.	**0.0403**	**0.0000**	**0.0038**	**0.0012**	**0.0235**	**0.0157**	**0.0224**	**0.2017**	**0.6913**	**0.9342**	**0.0000**	**0.0125**	**0.0119**	**0.0317**	**0.0055**	**0.0023**	**0.0018**	**0.0001**
c18c sim	0.0445	0.0000	0.0036	0.0007	0.0226	0.0152	0.0224	0.2000	0.6909	0.9327	0.0000	0.0129	0.0122	0.0324	0.0056	0.0023	0.0018	0.0002
c18d exp.	**0.0048**	**0.8021**	**0.0001**	**0.0000**	**0.0009**	**0.0014**	**0.0035**	**0.0410**	**0.1463**	**0.9237**	**0.0007**	**0.0115**	**0.0091**	**0.0349**	**0.0086**	**0.0048**	**0.0066**	**0.0001**
c18d sim	0.0005	0.8066	0.0001	0.0000	0.0008	0.0015	0.0035	0.0407	0.1463	0.9281	0.0010	0.0109	0.0086	0.0327	0.0080	0.0046	0.0060	0.0000
c18e exp.	**0.0056**	**0.8001**	**0.0001**	**0.0000**	**0.0012**	**0.0017**	**0.0040**	**0.0421**	**0.1452**	**0.9063**	**0.0009**	**0.0146**	**0.0118**	**0.0439**	**0.0108**	**0.0055**	**0.0060**	**0.0002**
c18e sim	0.0005	0.8059	0.0001	0.0000	0.0010	0.0017	0.0039	0.0409	0.1459	0.9095	0.0011	0.0141	0.0112	0.0420	0.0100	0.0055	0.0066	0.0000
c19a exp.	**0.0235**	**0.5615**	**0.0044**	**0.0005**	**0.0196**	**0.0123**	**0.0170**	**0.1533**	**0.2078**	**0.6412**	**0.0024**	**0.0641**	**0.0650**	**0.1700**	**0.0264**	**0.0123**	**0.0182**	**0.0004**
c19a sim	0.0217	0.5707	0.0028	0.0002	0.0197	0.0123	0.0168	0.1486	0.2073	0.6795	0.0028	0.0629	0.0569	0.1450	0.0240	0.0115	0.0170	0.0004
c19b exp.	**0.0067**	**0.6239**	**0.0022**	**0.0002**	**0.0143**	**0.0091**	**0.0122**	**0.1079**	**0.2235**	**0.6805**	**0.0016**	**0.0633**	**0.0577**	**0.1519**	**0.0233**	**0.0099**	**0.0115**	**0.0002**
c19b sim	0.0080	0.6248	0.0016	0.0001	0.0133	0.0086	0.0122	0.1079	0.2236	0.6893	0.0025	0.0618	0.0541	0.1436	0.0239	0.0103	0.0141	0.0004
c19c exp.	**0.0049**	**0.6420**	**0.0016**	**0.0001**	**0.0111**	**0.0072**	**0.0098**	**0.0850**	**0.2384**	**0.6913**	**0.0013**	**0.0617**	**0.0564**	**0.1489**	**0.0231**	**0.0080**	**0.0091**	**0.0002**
c19c sim	0.0041	0.6484	0.0011	0.0001	0.0106	0.0068	0.0098	0.0853	0.2338	0.7003	0.0023	0.0610	0.0524	0.1417	0.0224	0.0087	0.0108	0.0004
c19d exp.	**0.0143**	**0.3861**	**0.0037**	**0.0004**	**0.0255**	**0.0124**	**0.0151**	**0.1201**	**0.4223**	**0.7198**	**0.0024**	**0.0663**	**0.0662**	**0.1217**	**0.0143**	**0.0042**	**0.0047**	**0.0003**
c19d sim	0.0099	0.3887	0.0031	0.0005	0.0206	0.0120	0.0152	0.1243	0.4256	0.7371	0.0010	0.0589	0.0558	0.1237	0.0141	0.0045	0.0043	0.0005
c19e exp.	**0.0165**	**0.6733**	**0.0015**	**0.0001**	**0.0108**	**0.0055**	**0.0071**	**0.0571**	**0.2282**	**0.6182**	**0.0015**	**0.0940**	**0.0835**	**0.1658**	**0.0249**	**0.0059**	**0.0058**	**0.0003**
c19e sim	0.0014	0.6876	0.0007	0.0001	0.0071	0.0048	0.0067	0.0573	0.2342	0.7097	0.0021	0.0625	0.0520	0.1380	0.0210	0.0068	0.0076	0.0003

Table C3: Simulated and experimental equilibrium molar fractions of the extract phase, x^{I}_{i} and raffinate phase, x^{II}_{i}, for the system Hexane(1) + Water(2) + o-Tolunitrile(3) + m-Cresol(4) + p-Cresol(5) + Triethylene Glycol(6).

ID		x^{I}_{1}	x^{I}_{2}	x^{I}_{3}	x^{I}_{4}	x^{I}_{5}	x^{I}_{6}	x^{II}_{1}	x^{II}_{2}	x^{II}_{3}	x^{II}_{4}	x^{II}_{5}	x^{II}_{6}
mp1	**exp.**	**0.01754**	**0.39127**	**0.01538**	**0.07560**	**0.07422**	**0.42600**	**0.98145**	**0.00126**	**0.01201**	**0.00234**	**0.00295**	**0.00000**
mp1	sim.	0.02290	0.38687	0.01656	0.07945	0.07819	0.41602	0.98526	0.00040	0.01120	0.00119	0.00187	0.00008
mp2	**exp.**	**0.01393**	**0.60144**	**0.01196**	**0.06427**	**0.06555**	**0.24285**	**0.97988**	**0.00057**	**0.01363**	**0.00269**	**0.00323**	**0.00000**
mp2	sim.	0.01982	0.60059	0.01163	0.06451	0.06568	0.23776	0.98014	0.00072	0.01449	0.00231	0.00230	0.00004
mp3	**exp.**	**0.00546**	**0.65191**	**0.00724**	**0.03512**	**0.03672**	**0.26355**	**0.98014**	**0.00038**	**0.01604**	**0.00134**	**0.00177**	**0.00033**
mp3	sim.	0.00331	0.66002	0.00728	0.03617	0.03596	0.25727	0.98037	0.00069	0.01451	0.00195	0.00245	0.00004
mp4	**exp.**	**0.00934**	**0.64170**	**0.01017**	**0.04532**	**0.04596**	**0.24749**	**0.97705**	**0.00104**	**0.01684**	**0.00213**	**0.00250**	**0.00044**
mp4	sim.	0.00734	0.63414	0.01051	0.04752	0.04752	0.25298	0.97696	0.00072	0.01714	0.00234	0.00280	0.00004
mp5	**exp.**	**0.00795**	**0.63797**	**0.00911**	**0.04554**	**0.04634**	**0.25309**	**0.97876**	**0.00068**	**0.01587**	**0.00215**	**0.00240**	**0.00015**
mp5	sim.	0.00708	0.63862	0.00914	0.04705	0.04683	0.25128	0.97908	0.00071	0.01519	0.00228	0.00270	0.00004
mp6	**exp.**	**0.01056**	**0.63508**	**0.01251**	**0.04596**	**0.04610**	**0.24980**	**0.97190**	**0.00104**	**0.02239**	**0.00210**	**0.00238**	**0.00019**
mp6	sim.	0.00749	0.63143	0.01249	0.04793	0.04776	0.25290	0.97358	0.00075	0.02017	0.00249	0.00297	0.00004
mp7	**exp.**	**0.01186**	**0.63493**	**0.01435**	**0.04698**	**0.04665**	**0.24523**	**0.97044**	**0.00088**	**0.02401**	**0.00196**	**0.00239**	**0.00033**
mp7	sim.	0.00779	0.62781	0.01466	0.04853	0.04840	0.25280	0.97001	0.00077	0.02334	0.00265	0.00319	0.00004
mp8	**exp.**	**0.01413**	**0.37383**	**0.02132**	**0.08135**	**0.08206**	**0.42731**	**0.98396**	**0.00038**	**0.01275**	**0.00131**	**0.00160**	**0.00000**
mp8	sim.	0.02520	0.35949	0.02081	0.08268	0.08170	0.43011	0.98351	0.00038	0.01299	0.00116	0.00188	0.00009
mp9	**exp.**	**0.01485**	**0.54795**	**0.01299**	**0.05756**	**0.05770**	**0.30895**	**0.97835**	**0.00045**	**0.01711**	**0.00193**	**0.00216**	**0.00000**
mp9	sim.	0.01265	0.53963	0.01408	0.05952	0.05932	0.31481	0.97968	0.00060	0.01563	0.00177	0.00227	0.00005
mp10	**exp.**	**0.00741**	**0.69432**	**0.00791**	**0.03843**	**0.03814**	**0.21378**	**0.97626**	**0.00067**	**0.01848**	**0.00210**	**0.00248**	**0.00000**
mp10	sim.	0.00438	0.69910	0.00809	0.03944	0.03916	0.20982	0.97449	0.00081	0.01824	0.00297	0.00345	0.00003
mp11	**exp.**	**0.00815**	**0.69832**	**0.00831**	**0.03878**	**0.03891**	**0.20754**	**0.97519**	**0.00046**	**0.01932**	**0.00233**	**0.00270**	**0.00000**
mp11	sim.	0.00439	0.69910	0.00810	0.03935	0.03923	0.20983	0.97446	0.00081	0.01826	0.00296	0.00347	0.00003
mp12	**exp.**	**0.00478**	**0.74761**	**0.00713**	**0.03400**	**0.03344**	**0.17303**	**0.97671**	**0.00067**	**0.01694**	**0.00263**	**0.00305**	**0.00000**
mp12	sim.	0.00270	0.74573	0.00650	0.03325	0.03314	0.17869	0.97171	0.00089	0.01938	0.00365	0.00435	0.00003
mp13	**exp.**	**0.03949**	**0.61090**	**0.01207**	**0.05188**	**0.05180**	**0.23385**	**0.97469**	**0.00054**	**0.01976**	**0.00230**	**0.00263**	**0.00007**
mp13	sim.	0.01148	0.62226	0.01231	0.05490	0.05481	0.24423	0.97592	0.00074	0.01801	0.00251	0.00277	0.00004
mp14	**exp.**	**0.01002**	**0.61396**	**0.01515**	**0.06533**	**0.06495**	**0.23059**	**0.97402**	**0.00096**	**0.01920**	**0.00274**	**0.00293**	**0.00014**
mp14	sim.	0.02139	0.59354	0.01487	0.06678	0.06666	0.23677	0.97648	0.00075	0.01793	0.00246	0.00236	0.00004
mp15	**exp.**	**0.00659**	**0.57252**	**0.01767**	**0.08592**	**0.08555**	**0.23175**	**0.97076**	**0.00083**	**0.02094**	**0.00357**	**0.00390**	**0.00000**
mp15	sim.	0.04310	0.55279	0.01854	0.08235	0.08256	0.22065	0.97753	0.00075	0.01766	0.00227	0.00176	0.00003
mp16	**exp.**	**0.03468**	**0.49022**	**0.01790**	**0.09490**	**0.09472**	**0.26758**	**0.98011**	**0.00055**	**0.01323**	**0.00283**	**0.00316**	**0.00012**
mp16	sim.	0.06369	0.45751	0.01837	0.09911	0.09893	0.26239	0.98362	0.00062	0.01262	0.00169	0.00141	0.00005
mp17	**exp.**	**0.00546**	**0.64085**	**0.01196**	**0.07170**	**0.07315**	**0.19689**	**0.97828**	**0.00122**	**0.01376**	**0.00326**	**0.00344**	**0.00003**
mp17	sim.	0.02835	0.63207	0.01107	0.06948	0.07016	0.18886	0.97990	0.00080	0.01446	0.00270	0.00211	0.00003
mp18	**exp.**	**0.01278**	**0.69659**	**0.00901**	**0.05763**	**0.05758**	**0.16641**	**0.97389**	**0.00101**	**0.01643**	**0.00416**	**0.00442**	**0.00009**
mp18	sim.	0.01799	0.69072	0.00900	0.05927	0.05979	0.16323	0.97696	0.00087	0.01573	0.00350	0.00291	0.00002
mp19	**exp.**	**0.00792**	**0.69618**	**0.00666**	**0.03854**	**0.03964**	**0.21107**	**0.97971**	**0.00121**	**0.01470**	**0.00195**	**0.00236**	**0.00007**
mp19	sim.	0.00413	0.70313	0.00623	0.03807	0.03883	0.20961	0.97908	0.00078	0.01431	0.00266	0.00314	0.00003
mp20	**exp.**	**0.00252**	**0.74633**	**0.00519**	**0.03276**	**0.03274**	**0.18047**	**0.97969**	**0.00061**	**0.01481**	**0.00234**	**0.00252**	**0.00004**
mp20	sim.	0.00256	0.74894	0.00494	0.03275	0.03250	0.17830	0.97750	0.00084	0.01483	0.00319	0.00361	0.00003
mp21	**exp.**	**0.01044**	**0.62206**	**0.01078**	**0.05308**	**0.05400**	**0.24964**	**0.98125**	**0.00000**	**0.01467**	**0.00186**	**0.00218**	**0.00003**
mp21	sim.	0.01128	0.62244	0.00959	0.05423	0.05499	0.24747	0.98036	0.00071	0.01404	0.00228	0.00257	0.00004
mp22	**exp.**	**0.00326**	**0.66441**	**0.00638**	**0.02966**	**0.02948**	**0.26681**	**0.98377**	**0.00047**	**0.01138**	**0.00187**	**0.00210**	**0.00040**
mp22	sim.	0.00202	0.66575	0.00564	0.03017	0.02978	0.26665	0.98351	0.00065	0.01220	0.00157	0.00202	0.00004
mp23	**exp.**	**0.02300**	**0.57291**	**0.01442**	**0.08297**	**0.08305**	**0.22365**	**0.98075**	**0.00000**	**0.01431**	**0.00228**	**0.00260**	**0.00006**
mp23	sim.	0.04366	0.55493	0.01415	0.08268	0.08316	0.22142	0.98197	0.00072	0.01350	0.00212	0.00165	0.00003

Table C4. Simulated and experimental equilibrium molar fractions of the extract phase, x^{I}_{i} and raffinate phase, x^{II}_{i}, for the system Hexane(1) + Water(2) + Aniline(3) + o-Tolunitrile(4) + m-Cresol(5) + p-Cresol(6) + Triethylene Glycol(7).

ID		x^{I}_{1}	x^{I}_{2}	x^{I}_{3}	x^{I}_{4}	x^{I}_{5}	x^{I}_{6}	x^{I}_{7}	x^{II}_{1}	x^{II}_{2}	x^{II}_{3}	x^{II}_{4}	x^{II}_{5}	x^{II}_{6}	x^{II}_{7}
amp1	**exp.**	**0.0770**	**0.2711**	**0.0271**	**0.0211**	**0.1501**	**0.1754**	**0.2781**	**0.9800**	**0.0005**	**0.0021**	**0.0080**	**0.0038**	**0.0051**	**0.0005**
amp1	sim.	0.2074	0.2181	0.0243	0.0205	0.1316	0.1596	0.2386	0.9891	0.0005	0.0013	0.0072	0.0011	0.0009	0.0001
amp2	**exp.**	**0.0491**	**0.3300**	**0.0259**	**0.0188**	**0.1279**	**0.1142**	**0.3341**	**0.9818**	**0.0004**	**0.0024**	**0.0097**	**0.0027**	**0.0026**	**0.0003**
amp2	sim.	0.0967	0.3010	0.0251	0.0190	0.1236	0.1149	0.3197	0.9865	0.0005	0.0016	0.0087	0.0013	0.0013	0.0001
amp3	**exp.**	**0.0201**	**0.3456**	**0.0174**	**0.0153**	**0.1006**	**0.1315**	**0.3695**	**0.9852**	**0.0003**	**0.0016**	**0.0078**	**0.0019**	**0.0028**	**0.0003**
amp3	sim.	0.0823	0.3186	0.0174	0.0152	0.0973	0.1289	0.3402	0.9885	0.0004	0.0011	0.0074	0.0010	0.0015	0.0001
amp4	**exp.**	**0.0087**	**0.3988**	**0.0159**	**0.0119**	**0.0871**	**0.0680**	**0.4096**	**0.9788**	**0.0003**	**0.0013**	**0.0074**	**0.0014**	**0.0013**	**0.0094**
amp4	sim.	0.0226	0.3782	0.0153	0.0112	0.0874	0.0681	0.4172	0.9879	0.0004	0.0011	0.0076	0.0013	0.0017	0.0001
amp5	**exp.**	**0.0496**	**0.5306**	**0.0178**	**0.0093**	**0.0886**	**0.1214**	**0.1826**	**0.9809**	**0.0009**	**0.0027**	**0.0066**	**0.0034**	**0.0051**	**0.0003**
amp5	sim.	0.1010	0.5021	0.0169	0.0088	0.0835	0.1172	0.1705	0.9877	0.0008	0.0021	0.0067	0.0015	0.0012	0.0000
amp6	**exp.**	**0.0339**	**0.5800**	**0.0128**	**0.0063**	**0.0620**	**0.1109**	**0.1941**	**0.9817**	**0.0008**	**0.0021**	**0.0057**	**0.0023**	**0.0047**	**0.0026**
amp6	sim.	0.0652	0.5605	0.0125	0.0059	0.0607	0.1111	0.1841	0.9887	0.0007	0.0018	0.0057	0.0013	0.0017	0.0000
amp7	**exp.**	**0.0293**	**0.5723**	**0.0102**	**0.0060**	**0.0539**	**0.1121**	**0.2162**	**0.9869**	**0.0004**	**0.0015**	**0.0054**	**0.0018**	**0.0039**	**0.0001**
amp7	sim.	0.0558	0.5554	0.0100	0.0058	0.0534	0.1132	0.2065	0.9893	0.0007	0.0014	0.0056	0.0011	0.0019	0.0000
amp8	**exp.**	**0.0204**	**0.6553**	**0.0080**	**0.0038**	**0.0357**	**0.0523**	**0.2245**	**0.9882**	**0.0003**	**0.0017**	**0.0060**	**0.0012**	**0.0023**	**0.0002**
amp8	sim.	0.0080	0.6563	0.0079	0.0035	0.0373	0.0549	0.2321	0.9858	0.0007	0.0018	0.0063	0.0018	0.0035	0.0000
amp9	**exp.**	**0.0249**	**0.4215**	**0.0135**	**0.0008**	**0.0973**	**0.0600**	**0.3821**	**0.9959**	**0.0002**	**0.0010**	**0.0005**	**0.0014**	**0.0010**	**0.0001**
amp9	sim.	0.0234	0.4224	0.0133	0.0007	0.0974	0.0596	0.3832	0.9950	0.0004	0.0011	0.0005	0.0015	0.0014	0.0001
amp10	**exp.**	**0.0519**	**0.2794**	**0.0166**	**0.0019**	**0.1167**	**0.0725**	**0.4610**	**0.9961**	**0.0001**	**0.0008**	**0.0008**	**0.0011**	**0.0009**	**0.0001**
amp10	sim.	0.0357	0.2843	0.0168	0.0018	0.1189	0.0733	0.4693	0.9954	0.0003	0.0009	0.0009	0.0012	0.0013	0.0001
amp11	**exp.**	**0.0330**	**0.4203**	**0.0123**	**0.0008**	**0.0986**	**0.0608**	**0.3742**	**0.9958**	**0.0002**	**0.0010**	**0.0005**	**0.0014**	**0.0011**	**0.0000**
amp11	sim.	0.0250	0.4239	0.0124	0.0007	0.0993	0.0611	0.3776	0.9950	0.0004	0.0011	0.0005	0.0015	0.0013	0.0001
amp12	**exp.**	**0.0292**	**0.4394**	**0.0122**	**0.0008**	**0.0915**	**0.0563**	**0.3706**	**0.9954**	**0.0003**	**0.0010**	**0.0005**	**0.0014**	**0.0012**	**0.0002**
amp12	sim.	0.0205	0.4433	0.0122	0.0008	0.0923	0.0567	0.3742	0.9948	0.0004	0.0011	0.0006	0.0015	0.0014	0.0001

Table C5. Simulated and experimental equilibrium molar fractions of the extract phase, x^{I}_{i} and raffinate phase, x^{II}_{i}, for the system Hexane(1) + Water(2) + Indane(3) + Undecnae(4) + Naphthalene(5) + 2,4-Xylenol(6) + 3,4-Xylenol (7) + 3,5-Xylenol((8) + Triethylene Glycol(7).

ID		x^{I}_{1}	x^{I}_{2}	x^{I}_{3}	x^{I}_{4}	x^{I}_{5}	x^{I}_{6}	x^{I}_{7}	x^{I}_{8}	x^{I}_{9}	x^{II}_{1}	x^{II}_{2}	x^{II}_{3}	x^{II}_{4}	x^{II}_{5}	x^{II}_{6}	x^{II}_{7}	x^{II}_{8}	x^{II}_{9}
x1b	**exp.**	**0.00281**	**0.80705**	**0.00045**	**0.00028**	**0.00513**	**0.01924**	**0.01032**	**0.01039**	**0.14434**	**0.68555**	**0.00478**	**0.03137**	**0.08835**	**0.16699**	**0.01216**	**0.00470**	**0.00387**	**0.00222**
x1b	sim.	0.00002	0.81512	0.00026	0.00038	0.00558	0.01506	0.00915	0.01051	0.14391	0.66858	0.00486	0.03212	0.08828	0.16379	0.02346	0.00751	0.00467	0.00674
x1c	**exp.**	**0.00274**	**0.82080**	**0.00027**	**0.00016**	**0.00335**	**0.01380**	**0.00736**	**0.00740**	**0.14411**	**0.67844**	**0.00491**	**0.03489**	**0.09374**	**0.17105**	**0.00990**	**0.00317**	**0.00333**	**0.00058**
x1c	sim.	0.00002	0.81919	0.00027	0.00036	0.00586	0.01289	0.00708	0.00744	0.14689	0.68482	0.00480	0.03467	0.08973	0.15892	0.01310	0.00412	0.00353	0.00631
x1d	**exp.**	**0.00082**	**0.82532**	**0.00018**	**0.00001**	**0.00255**	**0.01091**	**0.00565**	**0.00561**	**0.14894**	**0.69772**	**0.00172**	**0.03255**	**0.08809**	**0.16305**	**0.00905**	**0.00305**	**0.00242**	**0.00235**
x1d	sim.	0.00002	0.82495	0.00023	0.00032	0.00546	0.01068	0.00566	0.00560	0.14707	0.70124	0.00453	0.03349	0.08875	0.15098	0.00944	0.00311	0.00266	0.00581
x1e	**exp.**	**0.00055**	**0.82616**	**0.00006**	**0.00001**	**0.00195**	**0.00754**	**0.00385**	**0.00378**	**0.15609**	**0.68943**	**0.00131**	**0.03334**	**0.09102**	**0.17068**	**0.00737**	**0.00237**	**0.00198**	**0.00251**
x1e	sim.	0.00002	0.83178	0.00019	0.00030	0.00538	0.00755	0.00391	0.00383	0.14705	0.70951	0.00451	0.03312	0.09264	0.14471	0.00607	0.00203	0.00183	0.00557
x2a	**exp.**	**0.00241**	**0.79780**	**0.00019**	**0.00005**	**0.00273**	**0.02542**	**0.01570**	**0.01575**	**0.13995**	**0.90243**	**0.00148**	**0.00867**	**0.02455**	**0.04782**	**0.00808**	**0.00315**	**0.00295**	**0.00087**
x2a	sim.	0.00002	0.79670	0.00015	0.00021	0.00066	0.02347	0.02007	0.01625	0.14247	0.90336	0.00130	0.00883	0.02432	0.04901	0.00855	0.00152	0.00265	0.00047
x2b	**exp.**	**0.00129**	**0.81622**	**0.00017**	**0.00034**	**0.00162**	**0.01565**	**0.00900**	**0.00930**	**0.14640**	**0.90534**	**0.00109**	**0.00886**	**0.02421**	**0.04881**	**0.00623**	**0.00226**	**0.00207**	**0.00112**
x2b	sim.	0.00002	0.81649	0.00010	0.00022	0.00069	0.01551	0.01028	0.00919	0.14750	0.90668	0.00127	0.00887	0.02433	0.04866	0.00623	0.00131	0.00205	0.00059
x2c	**exp.**	**0.00106**	**0.82618**	**0.00002**	**0.00003**	**0.00096**	**0.01166**	**0.00666**	**0.00660**	**0.14682**	**0.90889**	**0.00095**	**0.00910**	**0.02379**	**0.04827**	**0.00536**	**0.00186**	**0.00154**	**0.00023**
x2c	sim.	0.00002	0.82663	0.00008	0.00022	0.00066	0.01152	0.00729	0.00647	0.14710	0.90866	0.00126	0.00911	0.02428	0.04823	0.00506	0.00109	0.00166	0.00063
x2d	**exp.**	**0.00153**	**0.82869**	**0.00006**	**0.00002**	**0.00075**	**0.00909**	**0.00526**	**0.00530**	**0.14929**	**0.90978**	**0.00105**	**0.00894**	**0.02470**	**0.04776**	**0.00458**	**0.00155**	**0.00124**	**0.00041**
x2d	sim.	0.00002	0.83123	0.00007	0.00023	0.00067	0.00930	0.00563	0.00519	0.14767	0.90972	0.00126	0.00896	0.02451	0.04825	0.00428	0.00094	0.00140	0.00068
x2e	**exp.**	**0.00109**	**0.83258**	**0.00004**	**0.00003**	**0.00072**	**0.00667**	**0.00360**	**0.00360**	**0.15168**	**0.90860**	**0.00065**	**0.00911**	**0.02598**	**0.04856**	**0.00367**	**0.00122**	**0.00114**	**0.00107**
x2e	sim.	0.00002	0.83409	0.00006	0.00023	0.00069	0.00677	0.00384	0.00362	0.15067	0.91193	0.00125	0.00892	0.02479	0.04750	0.00317	0.00069	0.00101	0.00075
x3a	**exp.**	**0.00358**	**0.78636**	**0.00041**	**0.00007**	**0.00519**	**0.03036**	**0.01698**	**0.01758**	**0.13949**	**0.85132**	**0.00192**	**0.01387**	**0.03903**	**0.07403**	**0.01006**	**0.00397**	**0.00364**	**0.00216**
x3a	sim.	0.00002	0.79620	0.00021	0.00014	0.00129	0.02470	0.01800	0.01798	0.14146	0.85099	0.00179	0.01378	0.03803	0.07546	0.01259	0.00316	0.00314	0.00105
x3b	**exp.**	**0.00176**	**0.81048**	**0.00015**	**0.00001**	**0.00239**	**0.01795**	**0.00910**	**0.01048**	**0.14769**	**0.85328**	**0.00120**	**0.01443**	**0.03975**	**0.07577**	**0.00751**	**0.00353**	**0.00261**	**0.00192**
x3b	sim.	0.00002	0.81618	0.00014	0.00015	0.00133	0.01617	0.00988	0.01034	0.14580	0.85559	0.00177	0.01396	0.03835	0.07505	0.00879	0.00261	0.00257	0.00133
x3c	**exp.**	**0.00061**	**0.82014**	**0.00008**	**0.00005**	**0.00171**	**0.01284**	**0.00701**	**0.00722**	**0.15034**	**0.86111**	**0.00118**	**0.01426**	**0.03842**	**0.07489**	**0.00603**	**0.00204**	**0.00172**	**0.00035**
x3c	sim.	0.00002	0.82433	0.00011	0.00015	0.00138	0.01206	0.00697	0.00701	0.14797	0.85776	0.00176	0.01409	0.03838	0.07570	0.00680	0.00202	0.00200	0.00149
x3d	**exp.**	**0.00131**	**0.82901**	**0.00009**	**0.00005**	**0.00137**	**0.01049**	**0.00533**	**0.00544**	**0.14690**	**0.85939**	**0.00074**	**0.01406**	**0.03986**	**0.07556**	**0.00582**	**0.00181**	**0.00155**	**0.00120**
x3d	sim.	0.00002	0.83013	0.00010	0.00015	0.00132	0.01028	0.00538	0.00535	0.14728	0.86072	0.00175	0.01397	0.03862	0.07408	0.00604	0.00166	0.00164	0.00153
x3e	**exp.**	**0.00064**	**0.83062**	**0.00005**	**0.00003**	**0.00120**	**0.00725**	**0.00377**	**0.00378**	**0.15267**	**0.86294**	**0.00064**	**0.01415**	**0.03871**	**0.07186**	**0.00432**	**0.00133**	**0.00145**	**0.00461**
x3e	sim.	0.00002	0.83381	0.00008	0.00015	0.00133	0.00711	0.00376	0.00378	0.14996	0.86571	0.00171	0.01387	0.03805	0.07252	0.00418	0.00116	0.00119	0.00161
x4a	**exp.**	**0.00253**	**0.85678**	**0.00012**	**0.00002**	**0.00175**	**0.01665**	**0.00992**	**0.01104**	**0.10118**	**0.87167**	**0.00248**	**0.01093**	**0.03124**	**0.06175**	**0.01131**	**0.00462**	**0.00430**	**0.00171**
x4a	sim.	0.00001	0.86450	0.00007	0.00009	0.00030	0.01258	0.01003	0.01000	0.10240	0.87589	0.00150	0.01063	0.02963	0.05971	0.01322	0.00423	0.00468	0.00052
x4b	**exp.**	**0.00287**	**0.81553**	**0.00001**	**0.00004**	**0.00185**	**0.01726**	**0.00972**	**0.01039**	**0.14232**	**0.89029**	**0.00119**	**0.01060**	**0.02966**	**0.05666**	**0.00621**	**0.00219**	**0.00196**	**0.00124**
x4b	sim.	0.00002	0.81727	0.00011	0.00018	0.00087	0.01589	0.01015	0.00997	0.14556	0.88883	0.00143	0.01044	0.02924	0.05781	0.00738	0.00178	0.00229	0.00081
x4c	**exp.**	**0.00151**	**0.82105**	**0.00002**	**0.00005**	**0.00143**	**0.01257**	**0.00687**	**0.00711**	**0.14939**	**0.88738**	**0.00077**	**0.01115**	**0.03149**	**0.05962**	**0.00551**	**0.00182**	**0.00156**	**0.00069**
x4c	sim.	0.00002	0.82519	0.00009	0.00017	0.00093	0.01182	0.00706	0.00686	0.14787	0.88766	0.00146	0.01078	0.03135	0.05844	0.00598	0.00156	0.00178	0.00098
x4d	**exp.**	**0.00238**	**0.82551**	**0.00006**	**0.00001**	**0.00113**	**0.00984**	**0.00536**	**0.00535**	**0.15036**	**0.88408**	**0.00073**	**0.01151**	**0.03217**	**0.06277**	**0.00505**	**0.00161**	**0.00137**	**0.00070**
x4d	sim.	0.00002	0.83070	0.00008	0.00018	0.00090	0.00948	0.00543	0.00521	0.14800	0.89071	0.00143	0.01081	0.02998	0.05850	0.00489	0.00121	0.00147	0.00099

Table C5 (cont.)

ID		x'_1	x'_2	x'_3	x'_4	x'_5	x'_6	x'_7	x'_8	x'_9	x''_1	x''_2	x''_3	x''_4	x''_5	x''_6	x''_7	x''_8	x''_9
x4e	**exp.**	**0.00194**	**0.82124**	**0.00006**	**0.00002**	**0.00090**	**0.00711**	**0.00393**	**0.00391**	**0.16090**	**0.88983**	**0.00051**	**0.01123**	**0.03191**	**0.05921**	**0.00412**	**0.00147**	**0.00125**	**0.00048**
x4e	sim.	0.00002	0.82011	0.00008	0.00019	0.00118	0.00760	0.00427	0.00403	0.16252	0.89251	0.00142	0.01087	0.03132	0.05737	0.00344	0.00087	0.00100	0.00121
x5a	**exp.**	**0.00422**	**0.78312**	**0.00030**	**0.00005**	**0.00415**	**0.03095**	**0.01810**	**0.01874**	**0.14038**	**0.88415**	**0.00156**	**0.01131**	**0.03010**	**0.05838**	**0.00818**	**0.00318**	**0.00269**	**0.00046**
x5a	sim.	0.00002	0.79244	0.00019	0.00017	0.00089	0.02514	0.02024	0.01765	0.14328	0.88382	0.00147	0.01099	0.02962	0.05842	0.01023	0.00199	0.00281	0.00065
x5b	**exp.**	**0.00391**	**0.67329**	**0.00037**	**0.00003**	**0.00639**	**0.03308**	**0.01808**	**0.01746**	**0.24739**	**0.89362**	**0.00062**	**0.01129**	**0.02937**	**0.05667**	**0.00386**	**0.00126**	**0.00161**	**0.00169**
x5b	sim.	0.00004	0.68177	0.00042	0.00027	0.00346	0.03261	0.01878	0.01792	0.24473	0.89184	0.00128	0.01115	0.02962	0.05811	0.00421	0.00091	0.00130	0.00159
x5c	**exp.**	**0.00285**	**0.69460**	**0.00025**	**0.00002**	**0.00496**	**0.02339**	**0.01240**	**0.01264**	**0.24890**	**0.89358**	**0.00035**	**0.01084**	**0.03013**	**0.05716**	**0.00311**	**0.00094**	**0.00191**	**0.00200**
x5c	sim.	0.00005	0.69664	0.00030	0.00028	0.00351	0.02314	0.01293	0.01385	0.24932	0.89396	0.00126	0.01063	0.02982	0.05735	0.00336	0.00077	0.00110	0.00176
x5d	**exp.**	**0.00307**	**0.70026**	**0.00013**	**0.00002**	**0.00463**	**0.01888**	**0.01003**	**0.01016**	**0.25282**	**0.89162**	**0.00052**	**0.01144**	**0.03180**	**0.05973**	**0.00275**	**0.00092**	**0.00076**	**0.00045**
x5d	sim.	0.00005	0.70604	0.00025	0.00028	0.00355	0.01805	0.01014	0.00991	0.25172	0.89488	0.00125	0.01071	0.02987	0.05711	0.00278	0.00064	0.00089	0.00187
x5e	**exp.**	**0.00187**	**0.71516**	**0.00022**	**0.00001**	**0.00322**	**0.01274**	**0.00653**	**0.00675**	**0.25350**	**0.89498**	**0.00037**	**0.01102**	**0.03123**	**0.05850**	**0.00202**	**0.00066**	**0.00059**	**0.00063**
x5e	sim.	0.00005	0.71423	0.00020	0.00028	0.00354	0.01267	0.00671	0.00665	0.25566	0.89744	0.00122	0.01065	0.03014	0.05538	0.00207	0.00047	0.00064	0.00199
x6a	**exp.**	**0.00746**	**0.68664**	**0.00044**	**0.00014**	**0.00653**	**0.03136**	**0.01672**	**0.01757**	**0.23314**	**0.86435**	**0.00147**	**0.01373**	**0.03934**	**0.07159**	**0.00484**	**0.00132**	**0.00140**	**0.00197**
x6a	sim.	0.00005	0.68797	0.00044	0.00022	0.00493	0.03169	0.01735	0.01788	0.23949	0.86231	0.00159	0.01366	0.03896	0.07340	0.00486	0.00133	0.00142	0.00246
x6b	**exp.**	**0.00863**	**0.62526**	**0.00110**	**0.00008**	**0.01412**	**0.05898**	**0.03221**	**0.03389**	**0.22574**	**0.85718**	**0.00151**	**0.01452**	**0.04035**	**0.07494**	**0.00634**	**0.00201**	**0.00197**	**0.00119**
x6b	sim.	0.00004	0.63781	0.00096	0.00022	0.00485	0.05800	0.03324	0.03422	0.23067	0.85818	0.00166	0.01391	0.03873	0.07566	0.00645	0.00164	0.00170	0.00207
x6c	**exp.**	**0.00369**	**0.68557**	**0.00037**	**0.00011**	**0.00627**	**0.02461**	**0.01296**	**0.01354**	**0.25288**	**0.86524**	**0.00072**	**0.01448**	**0.04050**	**0.07211**	**0.00351**	**0.00124**	**0.00105**	**0.00115**
x6c	sim.	0.00005	0.69713	0.00036	0.00022	0.00509	0.02381	0.01291	0.01303	0.24740	0.86548	0.00154	0.01387	0.03851	0.07188	0.00386	0.00103	0.00117	0.00266
x6d	**exp.**	**0.00261**	**0.70526**	**0.00029**	**0.00001**	**0.00561**	**0.01727**	**0.01041**	**0.00975**	**0.24878**	**0.86670**	**0.00066**	**0.01428**	**0.03970**	**0.07244**	**0.00274**	**0.00097**	**0.00098**	**0.00155**
x6d	sim.	0.00006	0.70543	0.00029	0.00023	0.00525	0.01673	0.01056	0.00966	0.25179	0.86618	0.00153	0.01395	0.03872	0.07196	0.00293	0.00089	0.00095	0.00289
x6e	**exp.**	**0.00197**	**0.71542**	**0.00030**	**0.00002**	**0.00407**	**0.01302**	**0.00686**	**0.00694**	**0.25141**	**0.86381**	**0.00101**	**0.01456**	**0.04113**	**0.07287**	**0.00280**	**0.00092**	**0.00092**	**0.00199**
x6e	sim.	0.00006	0.71114	0.00025	0.00022	0.00518	0.01304	0.00690	0.00688	0.25634	0.87055	0.00148	0.01384	0.03915	0.06834	0.00233	0.00062	0.00071	0.00299
x7a	**exp.**	**0.00805**	**0.65137**	**0.00075**	**0.00034**	**0.00805**	**0.05119**	**0.02869**	**0.03036**	**0.22119**	**0.90820**	**0.00081**	**0.00881**	**0.02469**	**0.04728**	**0.00572**	**0.00209**	**0.00180**	**0.00060**
x7a	sim.	0.00003	0.64908	0.00063	0.00033	0.00228	0.05368	0.03414	0.03153	0.22831	0.90919	0.00118	0.00869	0.02444	0.04823	0.00504	0.00087	0.00149	0.00088
x7b	**exp.**	**0.00514**	**0.58344**	**0.00049**	**0.00004**	**0.00784**	**0.03000**	**0.01649**	**0.01636**	**0.34019**	**0.91404**	**0.00041**	**0.00897**	**0.02507**	**0.04633**	**0.00252**	**0.00090**	**0.00077**	**0.00100**
x7b	sim.	0.00009	0.58285	0.00053	0.00040	0.00504	0.03070	0.01733	0.01598	0.34707	0.91331	0.00090	0.00871	0.02444	0.04741	0.00204	0.00041	0.00072	0.00205
x7c	**exp.**	**0.00320**	**0.69730**	**0.00026**	**0.00005**	**0.00393**	**0.02247**	**0.01209**	**0.01216**	**0.24854**	**0.91012**	**0.00071**	**0.00894**	**0.02520**	**0.04801**	**0.00328**	**0.00111**	**0.00092**	**0.00171**
x7c	sim.	0.00005	0.70360	0.00025	0.00036	0.00258	0.02250	0.01275	0.01201	0.24590	0.91166	0.00111	0.00872	0.02454	0.04812	0.00303	0.00060	0.00099	0.00123
x7d	**exp.**	**0.00142**	**0.83201**	**0.00007**	**0.00004**	**0.00085**	**0.00691**	**0.00366**	**0.00376**	**0.15127**	**0.88953**	**0.00067**	**0.01113**	**0.03196**	**0.05902**	**0.00397**	**0.00124**	**0.00109**	**0.00139**
x7d	sim.	0.00002	0.83319	0.00007	0.00018	0.00094	0.00690	0.00377	0.00374	0.15119	0.89348	0.00142	0.01070	0.03031	0.05745	0.00360	0.00089	0.00107	0.00108
x7e	**exp.**	**0.00191**	**0.71573**	**0.00019**	**0.00003**	**0.00301**	**0.01263**	**0.00643**	**0.00652**	**0.25355**	**0.91144**	**0.00078**	**0.00911**	**0.02516**	**0.04723**	**0.00186**	**0.00062**	**0.00065**	**0.00314**
x7e	sim.	0.00005	0.71324	0.00019	0.00037	0.00274	0.01259	0.00687	0.00669	0.25725	0.91430	0.00107	0.00877	0.02468	0.04692	0.00184	0.00037	0.00061	0.00143
x8a	**exp.**	**0.00711**	**0.63997**	**0.00074**	**0.00008**	**0.01085**	**0.05578**	**0.03074**	**0.03189**	**0.22285**	**0.88783**	**0.00105**	**0.01083**	**0.03048**	**0.05719**	**0.00597**	**0.00211**	**0.00191**	**0.00263**
x8a	sim.	0.00004	0.64509	0.00074	0.00026	0.00318	0.05590	0.03400	0.03249	0.22830	0.88809	0.00137	0.01066	0.03007	0.05999	0.00575	0.00118	0.00158	0.00130
x8b	**exp.**	**0.00724**	**0.68616**	**0.00030**	**0.00013**	**0.00513**	**0.03104**	**0.01754**	**0.01711**	**0.23535**	**0.90901**	**0.00064**	**0.00885**	**0.02507**	**0.04736**	**0.00431**	**0.00150**	**0.00139**	**0.00187**
x8b	sim.	0.00004	0.68739	0.00034	0.00035	0.00247	0.03137	0.01941	0.01754	0.24110	0.91113	0.00113	0.00879	0.02430	0.04783	0.00378	0.00073	0.00123	0.00109

Table C5 (cont.)

ID		x'_1	x'_2	x'_3	x'_4	x'_5	x'_6	x'_7	x'_8	x'_9	x''_1	x''_2	x''_3	x''_4	x''_5	x''_6	x''_7	x''_8	x''_9
x8c	**exp.**	**0.00445**	**0.68096**	**0.00073**	**0.00011**	**0.01251**	**0.02553**	**0.01327**	**0.01354**	**0.24890**	**0.69841**	**0.00090**	**0.03221**	**0.09559**	**0.16218**	**0.00506**	**0.00166**	**0.00150**	**0.00250**
x8c	sim.	0.00011	0.68123	0.00081	0.00045	0.02195	0.02503	0.01300	0.01317	0.24424	0.71523	0.00407	0.03250	0.09467	0.13683	0.00497	0.00176	0.00177	0.00821
x8d	**exp.**	**0.00394**	**0.70109**	**0.00032**	**0.00029**	**0.00355**	**0.01808**	**0.00962**	**0.00978**	**0.25332**	**0.91350**	**0.00054**	**0.00908**	**0.02464**	**0.04748**	**0.00248**	**0.00077**	**0.00076**	**0.00075**
x8d	sim.	0.00005	0.70885	0.00022	0.00037	0.00259	0.01776	0.00989	0.00937	0.25090	0.91410	0.00108	0.00880	0.02418	0.04680	0.00247	0.00048	0.00082	0.00128
x8e	**exp.**	**0.00218**	**0.70861**	**0.00051**	**0.00001**	**0.00825**	**0.01396**	**0.00704**	**0.00705**	**0.25239**	**0.70889**	**0.00060**	**0.03287**	**0.09815**	**0.15214**	**0.00331**	**0.00099**	**0.00089**	**0.00217**
x8e	sim.	0.00011	0.70260	0.00054	0.00036	0.01876	0.01356	0.00687	0.00674	0.25047	0.74469	0.00344	0.03363	0.09953	0.10768	0.00276	0.00075	0.00095	0.00656
x9a	**exp.**	**0.01951**	**0.42564**	**0.00133**	**0.00047**	**0.01956**	**0.08237**	**0.04563**	**0.04780**	**0.35769**	**0.90914**	**0.00075**	**0.00889**	**0.02491**	**0.04724**	**0.00508**	**0.00184**	**0.00162**	**0.00053**
x9a	sim.	0.00008	0.42942	0.00208	0.00040	0.00594	0.09659	0.05640	0.05369	0.35540	0.91004	0.00081	0.00869	0.02462	0.04827	0.00363	0.00065	0.00119	0.00210
x9b	**exp.**	**0.01553**	**0.42465**	**0.00133**	**0.00026**	**0.01668**	**0.05740**	**0.03087**	**0.03174**	**0.42154**	**0.91282**	**0.00045**	**0.00883**	**0.02516**	**0.04514**	**0.00301**	**0.00120**	**0.00100**	**0.00239**
x9b	sim.	0.00013	0.42718	0.00141	0.00041	0.00767	0.06293	0.03470	0.03354	0.43203	0.91192	0.00068	0.00857	0.02461	0.04760	0.00236	0.00048	0.00089	0.00291
x9c	**exp.**	**0.01171**	**0.42831**	**0.00166**	**0.00021**	**0.01550**	**0.04490**	**0.02307**	**0.02321**	**0.45144**	**0.91889**	**0.00039**	**0.00854**	**0.02418**	**0.04399**	**0.00196**	**0.00073**	**0.00077**	**0.00055**
x9c	sim.	0.00015	0.43216	0.00114	0.00041	0.00812	0.04651	0.02466	0.02364	0.46321	0.91361	0.00064	0.00862	0.02464	0.04645	0.00176	0.00036	0.00068	0.00324
x9d	**exp.**	**0.01045**	**0.43402**	**0.00132**	**0.00022**	**0.01389**	**0.03395**	**0.01771**	**0.01813**	**0.47031**	**0.91743**	**0.00028**	**0.00859**	**0.02522**	**0.04327**	**0.00188**	**0.00064**	**0.00055**	**0.00213**
x9d	sim.	0.00016	0.44046	0.00096	0.00041	0.00811	0.03668	0.01927	0.01859	0.47534	0.91522	0.00063	0.00845	0.02455	0.04552	0.00143	0.00029	0.00055	0.00335
x9e	**exp.**	**0.00913**	**0.45247**	**0.00115**	**0.00018**	**0.01234**	**0.02498**	**0.01290**	**0.01234**	**0.47452**	**0.92161**	**0.00027**	**0.00851**	**0.02496**	**0.04197**	**0.00094**	**0.00024**	**0.00047**	**0.00102**
x9e	sim.	0.00017	0.45478	0.00078	0.00040	0.00800	0.02541	0.01326	0.01292	0.48429	0.91660	0.00062	0.00847	0.02481	0.04435	0.00104	0.00022	0.00041	0.00348
x10a	**exp.**	**0.01576**	**0.50487**	**0.00134**	**0.00010**	**0.01840**	**0.08031**	**0.04280**	**0.04193**	**0.29448**	**0.89071**	**0.00081**	**0.01089**	**0.03251**	**0.05593**	**0.00444**	**0.00191**	**0.00168**	**0.00112**
x10a	sim.	0.00006	0.51894	0.00152	0.00027	0.00587	0.08256	0.04799	0.04429	0.29850	0.88716	0.00118	0.01076	0.03226	0.05930	0.00467	0.00104	0.00134	0.00229
x10b	**exp.**	**0.01800**	**0.40809**	**0.00120**	**0.00038**	**0.01886**	**0.05939**	**0.03147**	**0.03216**	**0.43045**	**0.89736**	**0.00070**	**0.01092**	**0.02966**	**0.05454**	**0.00379**	**0.00125**	**0.00112**	**0.00068**
x10b	sim.	0.00015	0.41641	0.00168	0.00032	0.01060	0.06496	0.03453	0.03327	0.43808	0.89287	0.00077	0.01058	0.02988	0.05759	0.00257	0.00061	0.00094	0.00420
x10c	**exp.**	**0.01232**	**0.42688**	**0.00124**	**0.00014**	**0.01836**	**0.04361**	**0.02283**	**0.02340**	**0.45122**	**0.89905**	**0.00091**	**0.01070**	**0.03221**	**0.05304**	**0.00216**	**0.00080**	**0.00058**	**0.00055**
x10c	sim.	0.00017	0.42947	0.00124	0.00028	0.01126	0.04650	0.02426	0.02399	0.46282	0.89183	0.00076	0.01072	0.03236	0.05618	0.00198	0.00050	0.00073	0.00493
x10d	**exp.**	**0.01310**	**0.42447**	**0.00106**	**0.00016**	**0.01714**	**0.03564**	**0.01878**	**0.01890**	**0.47074**	**0.90113**	**0.00050**	**0.01061**	**0.03082**	**0.05177**	**0.00188**	**0.00071**	**0.00061**	**0.00197**
x10d	sim.	0.00018	0.43364	0.00107	0.00030	0.01111	0.03569	0.01928	0.01888	0.47983	0.89576	0.00073	0.01037	0.03061	0.05513	0.00152	0.00038	0.00059	0.00491
x10e	**exp.**	**0.01050**	**0.44581**	**0.00096**	**0.00038**	**0.01527**	**0.02431**	**0.01291**	**0.01285**	**0.47701**	**0.90257**	**0.00030**	**0.01155**	**0.03204**	**0.05048**	**0.00126**	**0.00038**	**0.00043**	**0.00099**
x10e	sim.	0.00019	0.45391	0.00096	0.00029	0.01069	0.02536	0.01335	0.01324	0.48201	0.89702	0.00073	0.01134	0.03086	0.05332	0.00115	0.00027	0.00045	0.00485
x11a	**exp.**	**0.03395**	**0.34950**	**0.00265**	**0.00074**	**0.03769**	**0.09732**	**0.05259**	**0.05240**	**0.37316**	**0.86260**	**0.00070**	**0.01375**	**0.03983**	**0.07110**	**0.00620**	**0.00202**	**0.00204**	**0.00177**
x11a	sim.	0.00012	0.37365	0.00354	0.00028	0.01406	0.11199	0.06054	0.05952	0.37631	0.86051	0.00103	0.01318	0.03854	0.07443	0.00436	0.00121	0.00142	0.00532
x11c	**exp.**	**0.01707**	**0.41163**	**0.00145**	**0.00051**	**0.02453**	**0.04591**	**0.02345**	**0.02349**	**0.45196**	**0.87244**	**0.00046**	**0.01351**	**0.03822**	**0.06799**	**0.00205**	**0.00062**	**0.00068**	**0.00403**
x11c	sim.	0.00020	0.43105	0.00148	0.00026	0.01567	0.04679	0.02427	0.02379	0.45649	0.86579	0.00095	0.01330	0.03878	0.07081	0.00214	0.00064	0.00081	0.00679
x11d	**exp.**	**0.01155**	**0.42391**	**0.00144**	**0.00017**	**0.02052**	**0.03605**	**0.01880**	**0.01870**	**0.46886**	**0.87081**	**0.00029**	**0.01381**	**0.04104**	**0.06935**	**0.00232**	**0.00081**	**0.00069**	**0.00088**
x11d	sim.	0.00021	0.43984	0.00128	0.00025	0.01545	0.03708	0.01939	0.01860	0.46791	0.86842	0.00093	0.01351	0.03908	0.06824	0.00175	0.00051	0.00066	0.00690
x11e	**exp.**	**0.01000**	**0.44512**	**0.00111**	**0.00006**	**0.01769**	**0.02585**	**0.01306**	**0.01293**	**0.47418**	**0.87456**	**0.00039**	**0.01379**	**0.04247**	**0.06572**	**0.00118**	**0.00038**	**0.00035**	**0.00117**
x11e	sim.	0.00021	0.45220	0.00100	0.00023	0.01457	0.02616	0.01334	0.01290	0.47938	0.87416	0.00089	0.01311	0.03965	0.06316	0.00128	0.00037	0.00047	0.00690

Table C5 (cont.)

ID	x^{I}_{1}	x^{I}_{2}	x^{I}_{3}	x^{I}_{4}	x^{I}_{5}	x^{I}_{6}	x^{I}_{7}	x^{I}_{8}	x^{I}_{9}	x^{II}_{1}	x^{II}_{2}	x^{II}_{3}	x^{II}_{4}	x^{II}_{5}	x^{II}_{6}	x^{II}_{7}	x^{II}_{8}	x^{II}_{9}
x12a exp.	**0.02967**	**0.37796**	**0.00195**	**0.00027**	**0.02641**	**0.09615**	**0.05168**	**0.05211**	**0.36378**	**0.89171**	**0.00107**	**0.01099**	**0.03120**	**0.05630**	**0.00456**	**0.00166**	**0.00142**	**0.00109**
x12a sim.	0.00010	0.39135	0.00274	0.00033	0.00911	0.10688	0.06002	0.05660	0.37287	0.89053	0.00085	0.01035	0.02997	0.05886	0.00395	0.00086	0.00128	0.00335
x12b exp.	**0.00181**	**0.86814**	**0.00006**	**0.00005**	**0.00086**	**0.01009**	**0.00586**	**0.00623**	**0.10689**	**0.88160**	**0.00186**	**0.01075**	**0.02971**	**0.05903**	**0.00966**	**0.00367**	**0.00317**	**0.00056**
x12b sim.	0.00001	0.87322	0.00005	0.00010	0.00030	0.00945	0.00628	0.00604	0.10454	0.88315	0.00148	0.01070	0.02951	0.05865	0.00978	0.00288	0.00325	0.00060
x12c exp.	**0.00136**	**0.87814**	**0.00004**	**0.00004**	**0.00054**	**0.00740**	**0.00403**	**0.00416**	**0.10429**	**0.88481**	**0.00184**	**0.01058**	**0.02951**	**0.05752**	**0.00887**	**0.00336**	**0.00288**	**0.00063**
x12c sim.	0.00001	0.87788	0.00004	0.00011	0.00029	0.00764	0.00458	0.00438	0.10507	0.88860	0.00146	0.01049	0.02915	0.05716	0.00792	0.00215	0.00246	0.00062
x12d exp.	**0.00087**	**0.87721**	**0.00012**	**0.00016**	**0.00047**	**0.00591**	**0.00343**	**0.00346**	**0.10837**	**0.88578**	**0.00151**	**0.01178**	**0.02988**	**0.05853**	**0.00710**	**0.00255**	**0.00210**	**0.00077**
x12d sim.	0.00001	0.88092	0.00005	0.00011	0.00029	0.00604	0.00374	0.00350	0.10535	0.89005	0.00145	0.01180	0.02909	0.05689	0.00632	0.00169	0.00207	0.00064
x12e exp.	**0.00220**	**0.87826**	**0.00003**	**0.00001**	**0.00035**	**0.00441**	**0.00246**	**0.00254**	**0.10974**	**0.89178**	**0.00149**	**0.01065**	**0.02977**	**0.05684**	**0.00552**	**0.00177**	**0.00158**	**0.00060**
x12e sim.	0.00001	0.88362	0.00004	0.00011	0.00030	0.00448	0.00258	0.00256	0.10631	0.89359	0.00146	0.01070	0.02903	0.05710	0.00465	0.00127	0.00150	0.00069
x13a exp.	**0.01447**	**0.60783**	**0.00150**	**0.00020**	**0.01956**	**0.06204**	**0.03234**	**0.03225**	**0.22981**	**0.80997**	**0.00159**	**0.01998**	**0.05645**	**0.09904**	**0.00746**	**0.00263**	**0.00241**	**0.00046**
x13a sim.	0.00004	0.63579	0.00136	0.00023	0.00817	0.06280	0.03334	0.03371	0.22455	0.80605	0.00237	0.01904	0.05407	0.10285	0.00751	0.00258	0.00203	0.00349
x13b exp.	**0.00621**	**0.66454**	**0.00074**	**0.00007**	**0.01126**	**0.03735**	**0.01853**	**0.01886**	**0.24243**	**0.81919**	**0.00099**	**0.01940**	**0.05455**	**0.09691**	**0.00481**	**0.00154**	**0.00140**	**0.00121**
x13b sim.	0.00006	0.67302	0.00069	0.00023	0.00911	0.03594	0.01806	0.01846	0.24443	0.81193	0.00221	0.01925	0.05408	0.09927	0.00551	0.00181	0.00163	0.00431
x13c exp.	**0.00457**	**0.68853**	**0.00050**	**0.00010**	**0.00829**	**0.02426**	**0.01249**	**0.01296**	**0.24830**	**0.81488**	**0.00087**	**0.01938**	**0.05454**	**0.09909**	**0.00372**	**0.00132**	**0.00122**	**0.00498**
x13c sim.	0.00006	0.69265	0.00047	0.00023	0.00886	0.02420	0.01273	0.01316	0.24764	0.81721	0.00213	0.01883	0.05346	0.09679	0.00428	0.00142	0.00133	0.00454
x13d exp.	**0.00421**	**0.68808**	**0.00038**	**0.00006**	**0.00774**	**0.01943**	**0.00993**	**0.01024**	**0.25992**	**0.80727**	**0.00142**	**0.02095**	**0.06054**	**0.10294**	**0.00368**	**0.00113**	**0.00092**	**0.00115**
x13d sim.	0.00006	0.70255	0.00039	0.00022	0.00832	0.01876	0.00991	0.00998	0.24982	0.82512	0.00203	0.01890	0.05283	0.09101	0.00351	0.00110	0.00109	0.00441
x13e exp.	**0.00475**	**0.69960**	**0.00033**	**0.00022**	**0.00593**	**0.01312**	**0.00683**	**0.00697**	**0.26225**	**0.82473**	**0.00119**	**0.01931**	**0.05425**	**0.09551**	**0.00224**	**0.00073**	**0.00065**	**0.00138**
x13e sim.	0.00007	0.70947	0.00033	0.00021	0.00860	0.01293	0.00684	0.00690	0.25467	0.82647	0.00201	0.01951	0.05508	0.08813	0.00254	0.00078	0.00080	0.00468
x14a exp.	**0.03820**	**0.33835**	**0.00406**	**0.00075**	**0.05360**	**0.10293**	**0.05396**	**0.05517**	**0.35298**	**0.81714**	**0.00117**	**0.01906**	**0.05547**	**0.09566**	**0.00586**	**0.00214**	**0.00196**	**0.00154**
x14a sim.	0.00018	0.36560	0.00481	0.00029	0.02455	0.11532	0.05926	0.06198	0.36801	0.80775	0.00153	0.01800	0.05514	0.10016	0.00481	0.00190	0.00168	0.00904
x14b exp.	**0.05162**	**0.00000**	**0.00000**	**0.00122**	**0.08061**	**0.10911**	**0.05568**	**0.05460**	**0.64715**	**0.85617**	**0.00000**	**0.00000**	**0.05551**	**0.08228**	**0.00303**	**0.00107**	**0.00095**	**0.00099**
x14b sim.	0.00346	0.00000	0.00000	0.00031	0.07947	0.12628	0.06367	0.06375	0.66308	0.84117	0.00000	0.00000	0.05390	0.08446	0.00202	0.00092	0.00062	0.01691
x14c exp.	**0.04368**	**0.00000**	**0.00000**	**0.00091**	**0.06480**	**0.08054**	**0.04039**	**0.04076**	**0.72892**	**0.89621**	**0.00000**	**0.00000**	**0.04154**	**0.05889**	**0.00165**	**0.00055**	**0.00051**	**0.00065**
x14c sim.	0.00250	0.00000	0.00000	0.00030	0.05346	0.08462	0.04278	0.04404	0.77230	0.88253	0.00000	0.00000	0.04054	0.06239	0.00132	0.00039	0.00039	0.01244
x14d exp.	**0.03126**	**0.00000**	**0.00000**	**0.00071**	**0.05932**	**0.06152**	**0.03090**	**0.03220**	**0.78409**	**0.89748**	**0.00000**	**0.00000**	**0.04191**	**0.05740**	**0.00110**	**0.00038**	**0.00026**	**0.00146**
x14d sim.	0.00261	0.00000	0.00000	0.00028	0.05204	0.06683	0.03403	0.03419	0.81002	0.88628	0.00000	0.00000	0.04130	0.05823	0.00103	0.00030	0.00030	0.01256
x14e exp.	**0.03666**	**0.00000**	**0.00000**	**0.00110**	**0.06015**	**0.04365**	**0.02167**	**0.02188**	**0.81489**	**0.86902**	**0.00000**	**0.00000**	**0.06619**	**0.06267**	**0.00078**	**0.00026**	**0.00025**	**0.00081**
x14e sim.	0.00375	0.00000	0.00000	0.00023	0.06792	0.04497	0.02245	0.02329	0.83740	0.86390	0.00000	0.00000	0.06495	0.05393	0.00066	0.00027	0.00020	0.01609
x15a exp.	**0.01239**	**0.37389**	**0.00207**	**0.00013**	**0.03240**	**0.06384**	**0.03273**	**0.03235**	**0.45019**	**0.88039**	**0.00040**	**0.01295**	**0.03926**	**0.06264**	**0.00240**	**0.00073**	**0.00061**	**0.00062**
x15a sim.	0.00019	0.39793	0.00208	0.00025	0.01643	0.06853	0.03417	0.03344	0.44698	0.86286	0.00094	0.01333	0.04001	0.07137	0.00282	0.00085	0.00103	0.00679
x15b exp.	**0.01661**	**0.38142**	**0.00204**	**0.00032**	**0.03906**	**0.06405**	**0.03214**	**0.03221**	**0.43217**	**0.82848**	**0.00055**	**0.01978**	**0.05747**	**0.08832**	**0.00276**	**0.00091**	**0.00082**	**0.00092**
x15b sim.	0.00026	0.40020	0.00246	0.00026	0.02693	0.06635	0.03344	0.03378	0.43631	0.81515	0.00138	0.01790	0.05804	0.09144	0.00303	0.00122	0.00118	0.01065
x15c exp.	**0.01134**	**0.41663**	**0.00184**	**0.00020**	**0.03443**	**0.04640**	**0.02338**	**0.02216**	**0.44361**	**0.83172**	**0.00069**	**0.02056**	**0.05906**	**0.08338**	**0.00210**	**0.00071**	**0.00080**	**0.00096**
x15c sim.	0.00028	0.42637	0.00193	0.00025	0.02631	0.04765	0.02464	0.02396	0.44862	0.81743	0.00138	0.01888	0.05808	0.08924	0.00238	0.00091	0.00095	0.01075

Table C5 (cont.)

ID	x^{I}_{1}	x^{I}_{2}	x^{I}_{3}	x^{I}_{4}	x^{I}_{5}	x^{I}_{6}	x^{I}_{7}	x^{I}_{8}	x^{I}_{9}	x^{II}_{1}	x^{II}_{2}	x^{II}_{3}	x^{II}_{4}	x^{II}_{5}	x^{II}_{6}	x^{II}_{7}	x^{II}_{8}	x^{II}_{9}
x15d exp.	**0.01507**	**0.43210**	**0.00167**	**0.00022**	**0.03111**	**0.03989**	**0.01838**	**0.01804**	**0.44354**	**0.84248**	**0.00081**	**0.01783**	**0.05595**	**0.07859**	**0.00163**	**0.00045**	**0.00054**	**0.00172**
x15d sim.	0.00027	0.43293	0.00162	0.00023	0.02432	0.03972	0.01854	0.01874	0.46362	0.82845	0.00126	0.01795	0.05541	0.08321	0.00196	0.00068	0.00075	0.01033
x15e exp.	**0.00893**	**0.44669**	**0.00138**	**0.00007**	**0.02227**	**0.02402**	**0.01251**	**0.01210**	**0.47203**	**0.84576**	**0.00085**	**0.01877**	**0.05761**	**0.07410**	**0.00114**	**0.00032**	**0.00032**	**0.00114**
x15e sim.	0.00027	0.44994	0.00124	0.00021	0.02186	0.02441	0.01264	0.01242	0.47702	0.83909	0.00117	0.01790	0.05426	0.07555	0.00129	0.00044	0.00051	0.00980
x16a exp.	**0.00380**	**0.78967**	**0.00055**	**0.00009**	**0.00602**	**0.03015**	**0.01757**	**0.01796**	**0.13419**	**0.79212**	**0.00256**	**0.02089**	**0.05463**	**0.10432**	**0.01161**	**0.00443**	**0.00377**	**0.00566**
x16a sim.	0.00001	0.80652	0.00024	0.00015	0.00199	0.02185	0.01540	0.01723	0.13661	0.79235	0.00245	0.02002	0.05246	0.10299	0.01807	0.00567	0.00405	0.00194
x16b exp.	**0.00203**	**0.80841**	**0.00021**	**0.00002**	**0.00309**	**0.01851**	**0.01055**	**0.01046**	**0.14673**	**0.80725**	**0.00168**	**0.01955**	**0.05336**	**0.10182**	**0.00991**	**0.00303**	**0.00259**	**0.00080**
x16b sim.	0.00002	0.81342	0.00019	0.00016	0.00232	0.01704	0.00978	0.01012	0.14696	0.80490	0.00240	0.01937	0.05206	0.10135	0.01071	0.00392	0.00293	0.00237
x16c exp.	**0.00144**	**0.81898**	**0.00015**	**0.00001**	**0.00223**	**0.01382**	**0.00730**	**0.00747**	**0.14859**	**0.80833**	**0.00142**	**0.02116**	**0.05329**	**0.10329**	**0.00728**	**0.00226**	**0.00199**	**0.00096**
x16c sim.	0.00002	0.82170	0.00016	0.00015	0.00234	0.01294	0.00696	0.00721	0.14852	0.80835	0.00238	0.02076	0.05281	0.09972	0.00848	0.00261	0.00237	0.00252
x16d exp.	**0.00249**	**0.82596**	**0.00057**	**0.00001**	**0.00178**	**0.01147**	**0.00546**	**0.00557**	**0.14669**	**0.80535**	**0.00121**	**0.01871**	**0.05725**	**0.10244**	**0.00816**	**0.00330**	**0.00229**	**0.00129**
x16d sim.	0.00002	0.82957	0.00013	0.00015	0.00230	0.01137	0.00539	0.00545	0.14563	0.80626	0.00250	0.01917	0.05663	0.10043	0.00779	0.00257	0.00191	0.00274
x16e exp.	**0.00374**	**0.83285**	**0.00048**	**0.00001**	**0.00137**	**0.00672**	**0.00371**	**0.00373**	**0.14740**	**0.76649**	**0.00106**	**0.01844**	**0.05593**	**0.14510**	**0.00701**	**0.00261**	**0.00143**	**0.00192**
x16e sim.	0.00002	0.83639	0.00010	0.00015	0.00215	0.00700	0.00379	0.00379	0.14661	0.81641	0.00238	0.01921	0.05309	0.09823	0.00483	0.00170	0.00141	0.00274

Table C6: Simulated and experimental equilibrium molar fractions of the extract phase, x^{I}_{i} and raffinate phase, x^{II}_{i}, for the system Hexane(1) + Water(2) + Mesitylene(3) + 5-Ethyl-2-methyl pyridine(4) + Aniline(5) + Benzonitrile(6) + Phenol(7) + Triethylene Glycol monomethylether(8)

ID		xI1	xI2	xI3	xI4	xI5	xI6	xI7	xI8	xII1	xII2	xII3	xII4	xII5	xII6	xII7	xII8
e1a	**exp.**	**0.0114**	**0.6262**	**0.0013**	**0.0061**	**0.0112**	**0.0085**	**0.1297**	**0.2056**	**0.9545**	**0.0014**	**0.0244**	**0.0061**	**0.0015**	**0.0045**	**0.0057**	**0.0021**
e1a	sim.	0.0185	0.6196	0.0015	0.0061	0.0112	0.0087	0.1275	0.2070	0.9554	0.0012	0.0244	0.0058	0.0014	0.0042	0.0060	0.0016
e1b	**exp.**	**0.0035**	**0.7781**	**0.0003**	**0.0030**	**0.0067**	**0.0045**	**0.0755**	**0.1283**	**0.9556**	**0.0012**	**0.0203**	**0.0069**	**0.0018**	**0.0053**	**0.0072**	**0.0016**
e1b	sim.	0.0044	0.7800	0.0004	0.0029	0.0067	0.0045	0.0748	0.1262	0.9542	0.0012	0.0201	0.0073	0.0018	0.0057	0.0079	0.0018
e1c	**exp.**	**0.0233**	**0.5336**	**0.0016**	**0.0103**	**0.0188**	**0.0137**	**0.2189**	**0.1798**	**0.9537**	**0.0013**	**0.0206**	**0.0068**	**0.0022**	**0.0052**	**0.0093**	**0.0009**
e1c	sim.	0.0328	0.5310	0.0017	0.0099	0.0190	0.0136	0.2133	0.1787	0.9544	0.0013	0.0202	0.0063	0.0022	0.0049	0.0097	0.0010
e1d	**exp.**	**0.0100**	**0.6271**	**0.0007**	**0.0056**	**0.0115**	**0.0089**	**0.1309**	**0.2053**	**0.9698**	**0.0011**	**0.0122**	**0.0051**	**0.0012**	**0.0041**	**0.0049**	**0.0016**
e1d	sim.	0.0180	0.6264	0.0007	0.0053	0.0109	0.0086	0.1248	0.2053	0.9692	0.0011	0.0123	0.0052	0.0013	0.0042	0.0053	0.0015
e1e	**exp.**	**0.0045**	**0.7862**	**0.0002**	**0.0025**	**0.0065**	**0.0039**	**0.0741**	**0.1221**	**0.9684**	**0.0011**	**0.0120**	**0.0056**	**0.0016**	**0.0044**	**0.0060**	**0.0008**
e1e	sim.	0.0043	0.7822	0.0002	0.0025	0.0068	0.0040	0.0734	0.1267	0.9649	0.0011	0.0124	0.0061	0.0018	0.0049	0.0072	0.0018
e2a	**exp.**	**0.0130**	**0.6638**	**0.0007**	**0.0040**	**0.0077**	**0.0059**	**0.0883**	**0.2166**	**0.9610**	**0.0013**	**0.0203**	**0.0059**	**0.0013**	**0.0035**	**0.0060**	**0.0007**
e2a	sim.	0.0136	0.6570	0.0010	0.0044	0.0081	0.0063	0.0893	0.2202	0.9644	0.0011	0.0189	0.0051	0.0010	0.0035	0.0040	0.0019
e2b	**exp.**	**0.0034**	**0.7990**	**0.0002**	**0.0023**	**0.0049**	**0.0035**	**0.0538**	**0.1329**	**0.9570**	**0.0017**	**0.0207**	**0.0069**	**0.0015**	**0.0049**	**0.0067**	**0.0006**
e2b	sim.	0.0030	0.8029	0.0003	0.0022	0.0049	0.0034	0.0535	0.1298	0.9579	0.0011	0.0197	0.0067	0.0014	0.0049	0.0061	0.0022
e2c	**exp.**	**0.0736**	**0.3790**	**0.0032**	**0.0082**	**0.0140**	**0.0110**	**0.1494**	**0.3617**	**0.9631**	**0.0012**	**0.0181**	**0.0045**	**0.0008**	**0.0025**	**0.0035**	**0.0065**
e2c	sim.	0.0408	0.3835	0.0034	0.0083	0.0143	0.0116	0.1564	0.3817	0.9679	0.0010	0.0179	0.0045	0.0008	0.0024	0.0031	0.0024
e2d	**exp.**	**0.0031**	**0.8576**	**0.0002**	**0.0021**	**0.0048**	**0.0031**	**0.0559**	**0.0731**	**0.9412**	**0.0020**	**0.0203**	**0.0113**	**0.0026**	**0.0076**	**0.0142**	**0.0007**
e2d	sim.	0.0011	0.8630	0.0001	0.0019	0.0048	0.0029	0.0552	0.0710	0.9411	0.0013	0.0198	0.0116	0.0027	0.0078	0.0137	0.0020
e2e	**exp.**	**0.0067**	**0.7498**	**0.0004**	**0.0040**	**0.0089**	**0.0058**	**0.0993**	**0.1250**	**0.9534**	**0.0015**	**0.0194**	**0.0077**	**0.0022**	**0.0058**	**0.0090**	**0.0010**
e2e	sim.	0.0064	0.7539	0.0004	0.0037	0.0089	0.0057	0.0980	0.1231	0.9537	0.0012	0.0187	0.0074	0.0022	0.0060	0.0093	0.0015
e3a	**exp.**	**0.0488**	**0.4317**	**0.0026**	**0.0117**	**0.0217**	**0.0162**	**0.2537**	**0.2135**	**0.9540**	**0.0009**	**0.0192**	**0.0065**	**0.0022**	**0.0053**	**0.0092**	**0.0027**
e3a	sim.	0.0448	0.4285	0.0026	0.0118	0.0222	0.0173	0.2580	0.2146	0.9565	0.0013	0.0189	0.0060	0.0020	0.0047	0.0097	0.0010
e3b	**exp.**	**0.0255**	**0.5566**	**0.0015**	**0.0089**	**0.0183**	**0.0126**	**0.2085**	**0.1680**	**0.9542**	**0.0011**	**0.0199**	**0.0066**	**0.0023**	**0.0052**	**0.0098**	**0.0010**
e3b	sim.	0.0302	0.5531	0.0015	0.0091	0.0181	0.0131	0.2062	0.1687	0.9545	0.0013	0.0198	0.0063	0.0022	0.0051	0.0099	0.0009
e3c	**exp.**	**0.0098**	**0.7196**	**0.0007**	**0.0054**	**0.0120**	**0.0083**	**0.1314**	**0.1128**	**0.9498**	**0.0013**	**0.0202**	**0.0078**	**0.0024**	**0.0061**	**0.0120**	**0.0004**
e3c	sim.	0.0099	0.7200	0.0005	0.0051	0.0117	0.0079	0.1324	0.1124	0.9475	0.0013	0.0206	0.0080	0.0027	0.0069	0.0119	0.0011
e3d	**exp.**	**0.0145**	**0.6281**	**0.0008**	**0.0056**	**0.0113**	**0.0081**	**0.1261**	**0.2055**	**0.9657**	**0.0009**	**0.0160**	**0.0054**	**0.0011**	**0.0040**	**0.0050**	**0.0018**
e3d	sim.	0.0168	0.6361	0.0009	0.0052	0.0111	0.0078	0.1212	0.2009	0.9657	0.0011	0.0154	0.0053	0.0014	0.0040	0.0055	0.0015
e3e	**exp.**	**0.0195**	**0.5750**	**0.0011**	**0.0075**	**0.0156**	**0.0103**	**0.1776**	**0.1934**	**0.9628**	**0.0009**	**0.0151**	**0.0059**	**0.0018**	**0.0043**	**0.0073**	**0.0018**
e3e	sim.	0.0252	0.5760	0.0011	0.0074	0.0152	0.0104	0.1697	0.1951	0.9641	0.0012	0.0147	0.0057	0.0017	0.0042	0.0072	0.0012

TableC6 (cont.).

ID		xl1	xl2	xl3	xl4	xl5	xl6	xl7	xl8	xl1	xl2	xl3	xl4	xl5	xl6	xl7	xl8
e4a	**exp.**	**0.0974**	**0.1746**	**0.0064**	**0.0212**	**0.0380**	**0.0285**	**0.4356**	**0.1983**	**0.9437**	**0.0013**	**0.0191**	**0.0065**	**0.0033**	**0.0053**	**0.0179**	**0.0028**
e4a	sim.	0.0700	0.1838	0.0063	0.0190	0.0396	0.0281	0.4466	0.2066	0.9434	0.0011	0.0188	0.0074	0.0032	0.0064	0.0191	0.0007
e4b	**exp.**	**0.0506**	**0.4388**	**0.0029**	**0.0142**	**0.0278**	**0.0193**	**0.3086**	**0.1378**	**0.9458**	**0.0014**	**0.0197**	**0.0071**	**0.0031**	**0.0057**	**0.0161**	**0.0012**
e4b	sim.	0.0548	0.4254	0.0026	0.0146	0.0279	0.0198	0.3139	0.1410	0.9474	0.0015	0.0201	0.0065	0.0030	0.0056	0.0153	0.0006
e4c	**exp.**	**0.0233**	**0.5998**	**0.0015**	**0.0106**	**0.0202**	**0.0141**	**0.2297**	**0.1007**	**0.9396**	**0.0016**	**0.0204**	**0.0087**	**0.0034**	**0.0067**	**0.0189**	**0.0005**
e4c	sim.	0.0278	0.6014	0.0009	0.0100	0.0203	0.0143	0.2262	0.0991	0.9451	0.0015	0.0200	0.0079	0.0033	0.0066	0.0151	0.0006
e4d	**exp.**	**0.0670**	**0.4094**	**0.0039**	**0.0171**	**0.0298**	**0.0217**	**0.3156**	**0.1357**	**0.9332**	**0.0016**	**0.0284**	**0.0083**	**0.0032**	**0.0067**	**0.0173**	**0.0013**
e4d	sim.	0.0563	0.4155	0.0038	0.0177	0.0298	0.0223	0.3155	0.1392	0.9358	0.0016	0.0281	0.0075	0.0033	0.0063	0.0168	0.0006
e4e	**exp.**	**0.0617**	**0.4295**	**0.0021**	**0.0128**	**0.0263**	**0.0184**	**0.3121**	**0.1371**	**0.9512**	**0.0015**	**0.0164**	**0.0062**	**0.0030**	**0.0054**	**0.0153**	**0.0010**
e4e	sim.	0.0550	0.4286	0.0020	0.0129	0.0267	0.0184	0.3175	0.1389	0.9537	0.0014	0.0156	0.0058	0.0029	0.0053	0.0148	0.0005
e5a	**exp.**	**0.0507**	**0.4310**	**0.0020**	**0.0119**	**0.0263**	**0.0170**	**0.3025**	**0.1584**	**0.9585**	**0.0012**	**0.0137**	**0.0053**	**0.0026**	**0.0047**	**0.0133**	**0.0007**
e5a	sim.	0.0528	0.4251	0.0018	0.0111	0.0266	0.0168	0.3095	0.1561	0.9581	0.0014	0.0139	0.0052	0.0027	0.0048	0.0134	0.0006
e5b	**exp.**	**0.0294**	**0.5415**	**0.0012**	**0.0079**	**0.0180**	**0.0121**	**0.2087**	**0.1813**	**0.9664**	**0.0011**	**0.0124**	**0.0051**	**0.0019**	**0.0044**	**0.0076**	**0.0011**
e5b	sim.	0.0312	0.5443	0.0010	0.0075	0.0178	0.0121	0.2073	0.1788	0.9644	0.0013	0.0130	0.0051	0.0020	0.0045	0.0089	0.0009
e5c	**exp.**	**0.0194**	**0.6115**	**0.0007**	**0.0072**	**0.0179**	**0.0110**	**0.2270**	**0.1053**	**0.9566**	**0.0014**	**0.0123**	**0.0055**	**0.0030**	**0.0053**	**0.0154**	**0.0005**
e5c	sim.	0.0262	0.6128	0.0005	0.0068	0.0181	0.0112	0.2219	0.1026	0.9583	0.0014	0.0122	0.0056	0.0028	0.0053	0.0137	0.0006
e5d	**exp.**	**0.0085**	**0.7211**	**0.0003**	**0.0045**	**0.0112**	**0.0063**	**0.1312**	**0.1170**	**0.9625**	**0.0012**	**0.0120**	**0.0053**	**0.0022**	**0.0051**	**0.0107**	**0.0010**
e5d	sim.	0.0097	0.7233	0.0003	0.0038	0.0108	0.0064	0.1324	0.1133	0.9611	0.0012	0.0122	0.0059	0.0023	0.0054	0.0108	0.0011
e5e	**exp.**	**0.0209**	**0.5466**	**0.0012**	**0.0088**	**0.0174**	**0.0118**	**0.2114**	**0.1820**	**0.9578**	**0.0012**	**0.0157**	**0.0061**	**0.0024**	**0.0051**	**0.0101**	**0.0015**
e5e	sim.	0.0310	0.5458	0.0012	0.0086	0.0183	0.0125	0.2077	0.1750	0.9606	0.0013	0.0154	0.0058	0.0021	0.0047	0.0093	0.0009
e6a	**exp.**	**0.0603**	**0.4286**	**0.0098**	**0.0212**	**0.0321**	**0.0263**	**0.2756**	**0.1462**	**0.9126**	**0.0023**	**0.0474**	**0.0084**	**0.0034**	**0.0062**	**0.0193**	**0.0005**
e6a	sim.	0.0487	0.4426	0.0062	0.0207	0.0318	0.0258	0.2768	0.1475	0.9071	0.0019	0.0508	0.0092	0.0040	0.0079	0.0183	0.0008
e6b	**exp.**	**0.0324**	**0.5890**	**0.0013**	**0.0069**	**0.0146**	**0.0099**	**0.1528**	**0.1931**	**0.9572**	**0.0014**	**0.0192**	**0.0069**	**0.0020**	**0.0049**	**0.0066**	**0.0018**
e6b	sim.	0.0225	0.5939	0.0013	0.0074	0.0150	0.0102	0.1554	0.1944	0.9591	0.0012	0.0189	0.0062	0.0018	0.0045	0.0071	0.0013

APPENDIX D: PRO II INPUT AND OUTPUT FILES

D1. Input files for Batch Extraction Flash Simulations

Listing D1.1 ProII Input File for Batch Extraction P1a Modelled with NRTLFit parameters

```
TITLE
 DIMENSION SI, temp=c,pres=kpa, STDTEMP=0, STDPRES=101.325
 PRINT  INPUT=ALL, STREAM=all, RATE=m,WT, wtfrac, MBALANCE
 SEQUENCE SIMSCI
 CALCULATION RVPBASIS=APIN, TVP=37.778

COMPONENT DATA
 LIBID 1,hexane/2,water/3,135mbenz/5,aniline/6,bnzntirl/7,phenol/8,teg
 NONLIB 4,etmepyr, FILL=SIMSCI
 STRUCTURE 4,1445(1),900(2),901(1)

THERMODYNAMIC DATA
 METHOD SYSTEM=NRTL, kval(lle)=nrtl, SET=nrtl01, DEFAULT
   kval(vle) fill=unifac
   kval(lle) fill=unifac
    nrtl3(K) 1,2,1883.50,  3579.90, 0.2
    nrtl3(K) 1,3,-1500.60, 6366.40, 0.2
    nrtl3(K) 1,4,2012.60,  5960.00, 0.2
    nrtl3(K) 1,5,481.50,   503.20,  0.2
    nrtl3(K) 1,6,2233.40,  -131.20, 0.2
    nrtl3(K) 1,7,1019.90,  84.91,   0.2
    nrtl3(K) 1,8,2164.50,  1559.0,  0.2
    nrtl3(K) 2,3,351.0,    750.50,  0.2
    nrtl3(K) 2,4,2996.20,  5230.90, 0.2
    nrtl3(K) 2,5,950.40,   62.630,  0.2
    nrtl3(K) 2,6,2602.80,  6205.80, 0.2
    nrtl3(K) 2,7,1403.20,  -211.3,  0.2
    nrtl3(K) 2,8,-248.00,  6668.6,  0.2
    nrtl3(K) 3,4,1445.50,  -199.3,  0.2
    nrtl3(K) 3,5,-139.90,  6691.50, 0.2
    nrtl3(K) 3,6,1758.8,   2330.30, 0.2
    nrtl3(K) 3,7,-261.30,  6656.40, 0.2
    nrtl3(K) 3,8,1326.60,  -1419.0, 0.2
    nrtl3(K) 4,5,-955.20,  1674.80, 0.2
    nrtl3(K) 4,6,2469.80,  2340.00, 0.2
    nrtl3(K) 4,7,1510.50,  1105.10, 0.2
    nrtl3(K) 4,8,2546.40,  1440.10, 0.2
    nrtl3(K) 5,6,1044.00,  -129.90, 0.2
    nrtl3(K) 5,7,1630.00,  -709.00, 0.2
    nrtl3(K) 5,8,278.60,   -450.30, 0.2
    nrtl3(K) 6,7,1057.70,  996.50,  0.2
    nrtl3(K) 6,8,3561.00,  1335.6,  0.2
    nrtl3(K) 7,8,-216.70,  -267.60, 0.2


STREAM DATA
 PROPERTY STREAM=S1, TEMPERATURE=40, PRESSURE=101.32, PHASE=M,&
     COMPOSITION(wt,kg/hr)=1,44.965/2,5.035/3,1.358/4,1.005/&
       5,1.010/6,1.041/7,10.657/8,15.026

UNIT OPERATIONS
 FLASH UID=F1
   FEED S1
   PRODUCT  L=S3, W=S4, V=S2
   ISOTHERMAL TEMPERATURE=40
END
```

D2. Input and Output Files for Pilot Plant Liquid-liquid Extraction Column

Listing D2.1 ProII Input File for Pilot plant test PP2 Modelled with NRTLFit parameters

```
TITLE
 DIMENSION SI, temp=c,pres=kpa, STDTEMP=0, STDPRES=101.325
 PRINT  INPUT=ALL, STREAM=all, RATE=m,WT, wtfrac, MBALANCE
 SEQUENCE SIMSCI
 CALCULATION RVPBASIS=APIN, TVP=37.778

COMPONENT DATA
 LIBID 1,hexane/2,water/3,aniline/4,otolntrl/5,mcresol/6,pcresol/7,teg

THERMODYNAMIC DATA
 METHOD SYSTEM=NRTL, kval(lle)=nrtl, SET=nrtl01, DEFAULT
   kval(vle) fill=unifac
   kval(lle) fill=unifac
    nrtl3(K) 1,2, 1883.500,  3579.900, 0.2
    nrtl3(K) 1,3, 481.50,     503.2000, 0.2
    nrtl3(K) 1,4, -83.020,    2566.880, 0.2
    nrtl3(K) 1,5, 2163.735,  -568.341, 0.2
    nrtl3(K) 1,6, 3411.378,  -867.235, 0.2
    nrtl3(K) 1,7, 2164.500,  1559.000, 0.2
    nrtl3(K) 2,3, 950.400,   62.63000, 0.2
    nrtl3(K) 2,4, 1070.770,   538.480, 0.2
    nrtl3(K) 2,5, 819.630,    270.035, 0.2
    nrtl3(K) 2,6, 1290.274,6799.999,  0.2
    nrtl3(K) 2,7, -248.000,  6668.600, 0.2
    nrtl3(K) 3,4, 3208.00,  4904.000,  0.2
    nrtl3(K) 3,5, -616.94,   1403.000,  0.2
    nrtl3(K) 3,6, 145.270,   -100.000,  0.2
    nrtl3(K) 3,7, 278.600,   -450.300,  0.2
    nrtl3(K) 4,5, 572.150,   -897.221,  0.2
    nrtl3(K) 4,6, 2283.992,-1082.295, 0.2
    nrtl3(K) 4,7, 2886.056, -366.289,  0.2
    nrtl3(K) 5,6, 1320.74,    -857.157,  0.2
    nrtl3(K) 5,7, 4578.407, -597.346,  0.2
    nrtl3(K) 6,7, 3453.312, 262.3960,  0.2

STREAM DATA
 PROPERTY STREAM=FSW1, TEMPERATURE=42.3, PRESSURE=101.32, PHASE=M,&
     COMPOSITION(wt,kg/hr)=1,0.616/2,0.750/3,0.224/4,0.054/5,1.865/ &
       6,1.246/7,11.114
 PROPERTY STREAM=COUNTER1, TEMPERATURE=42.3, PRESSURE=101.32, PHASE=M,&
     COMPOSITION(wt,kg/hr)=1,21.2


UNIT OPERATIONS

COLUMN UID=E1, NAME=LLEX1
 PARAMETER TRAY=7, LLEX=30, DAMP=1.0,ERRINC=100,CUTOFF=1.0E-8
 FEED FSW1,1/COUNTER1,7
 PRODUCT OVHD=RAFF1,100,BTMS=EXTRACT1
 PSPEC PTOP(KPA)=101.325,DPCOL(KPA)=45.5
 ESTIMATE MODEL=SIMPLE
 TEMPERATURE(C) 1,40/2,40/3,40/4,40/5,40/6,40/7,40
 PRINT PROPTABLES=brief
 METHOD SET=NRTL01
END
```

Listing D2.2 Excerpts from ProII Output File for Pilot plant test PP2 Modelled with NRTLFit parameters

==========COLUMN PROFILE==========

UNIT 1, 'E1', 'LLEX1'

TOTAL NUMBER OF ITERATIONS

LLEX METHOD 4

COLUMN SUMMARY

TRAY	TEMP DEG C	PRESSURE KPA	NET FLOW RATES L2 KG-MOL/HR	L1 KG-MOL/HR	FEED KG-MOL/HR	PRODUCT KG-MOL/HR	HEATER DUTIES M*KJ/HR
1	42.3	101.33	0.2		0.2L	0.2L	
2	42.3	108.91	0.2	0.2			
3	42.3	116.49	0.2	0.2			
4	42.3	124.07	0.2	0.2			
5	42.3	131.66	0.2	0.2			
6	42.3	139.24	0.2	0.2			
7	42.3	146.82	0.2	0.2L	0.2H		

==========MASS FLOWRATES OF PROCESS STREAMS==========

STREAM ID NAME PHASE	COUNTER1 LIQUID	EXTRACT1 LIQUID	FSW1 LIQUID	RAFF1 LIQUID
FLUID RATES, KG/HR				
1 HEXANE	21.2000	0.4069	0.6160	21.4091
2 WATER	0.0000	0.7487	0.7500	1.2651E-03
3 ANILINE	0.0000	0.2047	0.2240	0.0193
4 OTOLNTRL	0.0000	0.0129	0.0540	0.0411
5 MCRESOL	0.0000	1.8351	1.8650	0.0299
6 PCRESOL	0.0000	1.2079	1.2460	0.0381
7 TEG	0.0000	11.1100	11.1140	3.9574E-03
TOTAL RATE, KG/HR	21.2000	15.5263	15.8690	21.5427
TEMPERATURE, C	42.3000	42.3000	42.3000	42.3000
PRESSURE, KPA	101.3200	146.8250	101.3200	101.3250
ENTHALPY, M*KJ/HR	2.0200E-03	1.4236E-03	1.4545E-03	2.0509E-03
MOLECULAR WEIGHT	86.1780	103.0196	102.7641	86.2701
WEIGHT FRAC VAPOR	0.0000	0.0000	0.0000	0.0000
WEIGHT FRAC LIQUID	1.0000	1.0000	1.0000	1.0000

==========

D3. Input and Output Files for Proposed Process Including Solvent Recovery

Listing D3.1 ProII Input File for Proposed Process Flowsheet Modelled with NRTLFit parameters

```
TITLE $   proposed process with industrial type stream with solvent recovery
 SEQUENCE SIMSCI
 DIMENSION SI, TEMP=C, PRES=KPA, TIME=HR
 PRINT  INPUT=NONE, STREAM=all, RATE=WT, $PERCENTAGES=wt, MBALANCE
 CALCULATION RVPBASIS=APIN, TVP=37.778

COMPONENT DATA
 LIBID  1,HEXANE/ 2,WATER/ 3,TEG/ 4,PHENOL/ 5,MCRESOL/ 6,PCRESOL/7,24XYLNOL/ &
      8, 35XYLNOL/9, 34XYLNOL/10, ANILINE/11, OTOLUIDN/12, BNZNITRL/ &
      13, OTOLNTRL/15,135MBENZ/16,124MBENZ/17,INDANE/18,INDENE/ &
      19, NAPHTHLN/20,UNDECANE/21,DODECANE
 NONLIB 14,ETMEPYR, FILL=SIMSCI
 STRUCTURE 14,1445(1),900(2),901(1)

THERMODYNAMIC DATA
 METHOD SYSTEM(VLLE)=NRTL,KVAL(LLE)=NRTL &
       VISCOSITY(VL)=PETRO, SET=NRTL01,DEFAULT
   KVAL(VLE) FILL=UNIF, AZEOTROPE=SIMSCI
   KVAL(LLE) FILL=UNIF, AZEOTROPE=SIMSCI
            nrtl3(k)      1,      2,      1883.5,   3579.9,   0.2
            nrtl3(k)      1,      3,      2164.5,   1559,     0.2
            nrtl3(k)      1,      4,      1019.9,   84.91,    0.2
            nrtl3(k)      1,      5,      2163.7,   -568.3,   0.2
            nrtl3(k)      1,      6,      3411.4,   -867.2,   0.2
            nrtl3(k)      1,      7,      2276.2,   4526.2,   0.2
            nrtl3(k)      1,      8,      3852.8,   4099.8,   0.2
            nrtl3(k)      1,      9,      2798.5,   4831.7,   0.2
            nrtl3(k)      1,      10,     481.5,    503.2,    0.2
            nrtl3(k)      1,      11,     51.954,   622.62,   0.2
            nrtl3(k)      1,      12,     2233.4,   -131.2,   0.2
            nrtl3(k)      1,      13,     -83.02,   2566.9,   0.2
            nrtl3(k)      1,      14,     2012.6,   5960,     0.2
            nrtl3(k)      1,      15,     -1501,    6366.4,   0.2
            nrtl3(k)      1,      16,     -437.9,   1147.2,   0.2
            nrtl3(k)      1,      17,     662.8,    7109.7,   0.2
            nrtl3(k)      1,      18,     253.27,   -375.3,   0.2
            nrtl3(k)      1,      19,     231.44,   -326.2,   0.2
            nrtl3(k)      1,      20,     -2142,    5842.7,   0.2
            nrtl3(k)      1,      21,     4451.3,   -1369,    0.2
            nrtl3(k)      2,      3,      -248,     6668.6,   0.2
            nrtl3(k)      2,      4,      1403.2,   -211.3,   0.2
            nrtl3(k)      2,      5,      819.63,   270.04,   0.2
            nrtl3(k)      2,      6,      1290.3,   6800,     0.2
            nrtl3(k)      2,      7,      2544.8,   5852.9,   0.2
            nrtl3(k)      2,      8,      3283.3,   2930.2,   0.2
            nrtl3(k)      2,      9,      3178.4,   3969.4,   0.2
            nrtl3(k)      2,      10,     950.4,    62.63,    0.2
            nrtl3(k)      2,      11,     884.57,   4488.9,   0.2
            nrtl3(k)      2,      12,     2602.8,   6205.8,   0.2
            nrtl3(k)      2,      13,     1070.8,   538.48,   0.2
            nrtl3(k)      2,      14,     2996.2,   5230.9,   0.2
            nrtl3(k)      2,      15,     351,      750.5,    0.2
            nrtl3(k)      2,      16,     4457.2,   4746.2,   0.2
            nrtl3(k)      2,      17,     2351,     4756.2,   0.2
            nrtl3(k)      2,      18,     4043.8,   636.41,   0.2
            nrtl3(k)      2,      19,     3817,     699.93,   0.2
            nrtl3(k)      2,      20,     1842.8,   3365.8,   0.2
            nrtl3(k)      2,      21,     6977,     434,      0.2
            nrtl3(k)      3,      4,      -267.6,   -216.7,   0.2
            nrtl3(k)      3,      5,      -597.3,   4578.4,   0.2
            nrtl3(k)      3,      6,      262.4,    3453.3,   0.2
            nrtl3(k)      3,      7,      334.66,   3932.5,   0.2
            nrtl3(k)      3,      8,      785.22,   2850.1,   0.2
            nrtl3(k)      3,      9,      876.55,   2176.4,   0.2
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```
      nrtl3(k)    3,    10,    -450.3,   278.6,   0.2
      nrtl3(k)    3,    11,    -969.7,   1265.3,  0.2
      nrtl3(k)    3,    12,    1335.6,   3561,    0.2
      nrtl3(k)    3,    13,    -366.3,   2886.1,  0.2
      nrtl3(k)    3,    14,    1440.1,   2546.4,  0.2
      nrtl3(k)    3,    15,    -1419,    1326.6,  0.2
      nrtl3(k)    3,    16,    472.06,   5835.4,  0.2
      nrtl3(k)    3,    17,    356.75,   -68.27,  0.2
      nrtl3(k)    3,    18,    -409.6,   487.42,  0.2
      nrtl3(k)    3,    19,    -359.8,   536.95,  0.2
      nrtl3(k)    3,    20,    -1581,    4254.8,  0.2
      nrtl3(k)    3,    21,    -67.09,   1382,    0.2
      nrtl3(k)    4,    10,    -709,     1630,    0.2
      nrtl3(k)    4,    12,    996.5,    1057.7,  0.2
      nrtl3(k)    4,    14,    1105.1,   1510.5,  0.2
      nrtl3(k)    4,    15,    6656.4,   -261.3,  0.2
      nrtl3(k)    5,    6,     1320.7,   -857.2,  0.2
      nrtl3(k)    5,    10,    1403,     -616.9,  0.2
      nrtl3(k)    5,    11,    -788.8,   38.469,  0.2
      nrtl3(k)    5,    13,    -897.2,   572.15,  0.2
      nrtl3(k)    5,    16,    152.37,   1871.9,  0.2
      nrtl3(k)    5,    18,    -598.5,   3276,    0.2
      nrtl3(k)    5,    20,    4720.9,   340.62,  0.2
      nrtl3(k)    6,    10,    -100,     145.27,  0.2
      nrtl3(k)    6,    13,    -1082,    2284,    0.2
      nrtl3(k)    7,    8,     2602.1,   2082.2,  0.2
      nrtl3(k)    7,    9,     2100,     1775.4,  0.2
      nrtl3(k)    7,    17,    -856.6,   846.48,  0.2
      nrtl3(k)    7,    19,    7457.9,   9086.9,  0.2
      nrtl3(k)    7,    21,    540.55,   9100.2,  0.2
      nrtl3(k)    8,    9,     2574.9,   2488.5,  0.2
      nrtl3(k)    8,    17,    933.42,   4356.9,  0.2
      nrtl3(k)    8,    19,    990.98,   2556.5,  0.2
      nrtl3(k)    8,    21,    -157.3,   4963,    0.2
      nrtl3(k)    9,    17,    598.99,   828.3,   0.2
      nrtl3(k)    9,    19,    1170,     1953,    0.2
      nrtl3(k)    9,    21,    3294.9,   5256,    0.2
      nrtl3(k)    10,   12,    1044,     -129.9,  0.2
      nrtl3(k)    10,   13,    3208,     4904,    0.2
      nrtl3(k)    10,   14,    1674.8,   -955.2,  0.2
      nrtl3(k)    10,   15,    6691.5,   -139.9,  0.2
      nrtl3(k)    11,   13,    -372.3,   -1950,   0.2
      nrtl3(k)    11,   16,    -1003,    15.291,  0.2
      nrtl3(k)    11,   18,    -297.6,   283.68,  0.2
      nrtl3(k)    11,   20,    -440.5,   -324.5,  0.2
      nrtl3(k)    12,   14,    2340,     2469.8,  0.2
      nrtl3(k)    12,   15,    2330.3,   1758.8,  0.2
      nrtl3(k)    13,   16,    3765,     -71.69,  0.2
      nrtl3(k)    13,   18,    -402.8,   572.44,  0.2
      nrtl3(k)    13,   20,    6190,     -780.2,  0.2
      nrtl3(k)    14,   15,    -199.3,   1445.5,  0.2
      nrtl3(k)    16,   18,    876.64,   -1976,   0.2
      nrtl3(k)    16,   20,    4392,     -1843,   0.2
      nrtl3(k)    17,   19,    475,      2685,    0.2
      nrtl3(k)    17,   21,    348.86,   -602,    0.2
      nrtl3(k)    18,   20,    4502.6,   -1057,   0.2
      nrtl3(k)    19,   21,    4016,     119,     0.2

METHOD SYSTEM=NRTL, SET=NRTL02
    KVAL(VLE)  FILL=UNIFAC, AZEOTROPE=SIMSCI
  METHOD SYSTEM(VLE)=WILSON, SET=WILSON03, TRANSPORT=PETRO
    KVAL(VLE)  FILL=UNIFAC, AZEOTROPE=SIMSCI

STREAM DATA

 PROP STREAM=FEED_EX,TEMP=40,RATE(KG/HR)=3000,PRES=101.325, PHASE=M &
   COMP(KG/HR)=4,22.7/5,28.8/6,0.0/7,2.6/8,1.9/9,1.9/10,0.1/11,0.15/&
       12,0.6/13,1.5/14,1.3/15,3.3/16,3.1/17,1.5/18,3.0/ &
       19,13.9/20,3.6/21,10.5, NORMALIZE
```

```
 PROP STREAM=SOLV_EX,TEMP=40,RATE(KG/HR)=11689.5,PRES=101.325, PHASE=M &
   COMP(KG/HR)=2,75.9/3,304.7/4,2.354/5,2.8502/7,0.2604/8,1.1643/ &
        9,2.3053/10,0.0270/11,0.0286/12,0.0399/13,0.005/  &
        14,0.005, NORMALIZE
 PROP STREAM=HEX_EX,TEMP=40,RATE(KG/HR)=15090,PRES=101.325, PHASE=M &
   COMP(KG/HR)=1,500/2,3.031/3,0.0169/12,0.002, NORMALIZE
 PROP STREAM=REFLUX1,TEMP=40,RATE(KG/HR)=150,PRES=101.325, PHASE=M &
   COMP(KG/HR)=2,42.5, NORMALIZE


UNIT OPERATION DATA

 COLUMN UID=E1, NAME=LLEX1
   PARAMETER TRAY=7, LLEX=30, DAMP=1.0,ERRINC=100,CUTOFF=1.0E-8
   FEED FEED_EX,1/SOLV_EX,1/HEX_EX,7
   PRODUCT OVHD=RAFF1,100,BTMS=EXTRACT1
   TFLOW NET(L1)=1,1/2,2/3,3/4,4/5,5/6,6/7,7
   TFLOW NET(L2)=11,1/22,2/33,3/44,4/55,5/66,6/77,7
   PSPEC PTOP(KPA)=101.325,DPCOL(KPA)=45.5
   ESTIMATE MODEL=SIMPLE
   TEMPERATURE(C) 1,40/2,40/3,40/4,40/5,40/6,40/7,40
   PRINT PROPTABLES=ALL
   METHOD SET=NRTL01

 FLASH UID=HEX_MIX
   FEED HEX_WASH2, RAFF1
   PRODUCT L=RAFF2
   ISOTHERMAL TEMP 40, PRESS(KPA)=101.325
   METHOD SET=NRTL01

 COLUMN UID=HEX_REC
   PARAMETER TRAY=13, SURE=100
   FEED RAFF2,8
   PRODUCT OVHD(KG/H)=HEX_DIST,14985, BTMS=NOILS
   CONDENSER TYPE=BUBB, PRES(KPA)=101.325
   DUTY 1,1/2,13
   PSPEC PTOP(KPA)=101.325, DPTRAY(KPA)=1
   ESTIMATE MODEL=CHEM, RRATIO=0.5, TTEMP=68, BTEMP=210
   SPEC STREAM=HEX_DIST,RATE(KG/H), VALUE=15810, ATOL=90.0
   SPEC RRATIO,Value=0.5
   VARIABLE DUTY=1,2
   PRINT PROPTABLES=ALL
   TSIZE
$  ESTIMATE MODEL=REFINING, RRATIO=0.8
   REBOILER TYPE=KETTLE
   METHOD SET=WILSON03

 SPLITTER UID=HEX_SPLIT
   FEED=HEX_DIST
   PRODUCT L=HEX_WASH, L=HEX_RECYC
   SPEC STREAM=HEX_WASH, RATE(KG/H), VALUE=750 $, DIVIDE, &
        $REFFEED, VALUE=0.05
   METHOD SET=WILSON03

 FLASH UID=WR_WASH
   FEED HEX_WASH, WR_DIST4
   PRODUCT L=HEX_WASH2, W=WR_DIST2
   ISOTHERMAL TEMP 40, PRESS(KPA)=20
   METHOD SET=NRTL01

 COLUMN UID=WATER_REC
   PARAMETER TRAY=6, SURE=150
   FEED REFLUX1,1/EXTRACT1,4
   PRODUCT OVHD(KG/H)=WR_DIST,BTMS=WR_BTMS,8634
   DUTY 1,6
   PSPEC PTOP(KPA)=20, DPTRAY(KPA)=0.35
   ESTIMATE MODEL=CHEM, RRATIO=0.25, TTEMP=20, BTEMP=210
   SPEC STREAM=WR_BTMS,COMP=2,RATE(KG/H), VALUE=0.9
   VARIABLE DUTY=1
   PRINT PROPTABLES=BRIEF
   TSIZE
   METHOD SET=WILSON03
```

```
 FLASH UID=WR_COND NAME=PSEUDO CONDENSER
  FEED WR_DIST
  PRODUCT L=WR_DIST4, V=FLARE
  ISOTHERMAL TEMP 40, PRESS(KPA)=20
  METHOD SET=WILSON03

 SPLITTER UID=WR_REFLUX
  FEED=WR_DIST2
  PRODUCT L=REFLUX1, L=WR_DIST3
  SPEC STREAM=REFLUX1, RATE(KG/H), DIVIDE, &
       REFFEED, VALUE=0.5
  METHOD SET=WILSON03

 COLUMN UID=TEG_REC
  PARAMETER TRAY=7, SURE=150
  FEED WR_BTMS,4
  PRODUCT OVHD(KG/H)=PHENOLICS,BTMS=TRIEG,9180
  CONDENSER TYPE=BUBB, PRES(KPA)=2
  DUTY 1,1/2,7
  PSPEC PTOP(KPA)=2, DPTRAY(KPA)=1
  ESTIMATE MODEL=CHEM, RRATIO=0.25, TTEMP=40, BTEMP=200
  SPEC STREAM=PHENOLICS,COMP=3,RATE(KG/H), VALUE=0.3
  SPEC STREAM=TRIEG,RATE(KG/H), VALUE=9300
  VARIABLE DUTY=1,2
  PRINT PROPTABLES=BRIEF
  METHOD SET=WILSON03
$  TSIZE
  PACKING SULZER=M250X, HETP=0.6

 FLASH UID=SOLV_MIX
  FEED TRIEG, WR_DIST3
  PRODUCT L=SOL_EX_OUT
  ISOTHERMAL TEMP 40, PRESS(KPA)=101.325
  METHOD SET=NRTL01

END
```

Listing D3.2 Excerpts from ProII Output File for Proposed Process Flowsheet Modelled with NRTLFit parameters

FLASH DRUM SUMMARY

FLASH ID	WR_COND	
NAME	PSEUDO CONDENSER	
FEEDS	WR_DIST	
PRODUCTS VAPOR	FLARE	
LIQUID	WR_DIST4	
TEMPERATURE, C	40.000	
PRESSURE, KPA	20.000	
PRESSURE DROP, KPA	0.000	
MOLE FRAC VAPOR	4.02313E-04	
MOLE FRAC LIQUID	0.99960	
DUTY, M*KJ/HR	-11.47963	
FLASH TYPE	ISOTHERMAL	

FLASH ID	HEX_MIX	WR_WASH	SOLV_MIX
NAME			
FEEDS	HEX_WASH2 RAFF1	HEX_WASH WR_DIST4	TRIEG WR_DIST3
PRODUCTS LIQUID 1	RAFF2	HEX_WASH2	SOL_EX_OUT
LIQUID 2	WR_DIST2		
TEMPERATURE, C	40.000	40.000	40.000
PRESSURE, KPA	101.325	20.000	101.325
PRESSURE DROP, KPA	-81.325	0.000	-94.325
MOLE FRAC VAPOR	0.00000	0.05219	0.00000
MOLE FRAC TOTAL LIQUID	1.00000	0.94781	1.00000
MOLE FRAC LIQUID 1	0.97407	0.00173	0.00128
MOLE FRAC LIQUID 2	0.02593	0.94608	0.99872
DUTY, M*KJ/HR	-0.49830	0.46013	-3.50568
FLASH TYPE	ISOTHERMAL	ISOTHERMAL	ISOTHERMAL

UNIT 1, 'E1', 'LLEX1'

COLUMN SUMMARY

TRAY		TEMP DEG C	PRESSURE KPA		NET FLOW RATES L2	L1	FEED	PRODUCT	HEATER DUTIES
					KG-MOL/HR				M*KJ/HR
1	40.0	101.33		207.4	26.2L	183.9L			
							189.8L		
2		40.0	108.91		206.9	175.3			
3		40.0	116.49		206.8	174.8			
4		40.0	124.07		206.7	174.7			
5		40.0	131.66		206.7	174.7			
6		40.0	139.24		206.7	174.6			
7		40.0	146.82			174.6	179.1L	211.2H	

UNIT 3, 'HEX_REC'

TOTAL NUMBER OF ITERATIONS

SURE METHOD 44

COLUMN SUMMARY

TRAY	TEMP DEG C	PRESSURE KPA		NET FLOW RATES LIQUID	VAPOR	FEED	PRODUCT	HEATER DUTIES
				KG-MOL/HR				M*KJ/HR
1C	61.4	101.33		93.8			187.7L	-8.6496
2	67.8	101.33		98.4	281.5			
3	68.4	102.33		98.4	286.1			
4	68.7	103.33		98.2	286.1			
5	69.1	104.33		97.9	285.8			
6	69.4	105.33		97.6	285.6			
7	69.7	106.33		96.0	285.3			
8	70.9	107.33	339.6	283.7	198.4L			
9	71.8	108.33	341.2	328.9				
10	72.2	109.33	338.6	330.5				
11	74.0	110.33	294.7	328.0				
12	100.5	111.33	187.4	284.0				
13R	174.9	112.33			176.7		10.7L	9.8467

TRAY SIZING MECHANICAL DATA

SECTION	TRAY NUMBERS	TRAY PASSES	TRAY SPACING MM	SYSTEM FACTOR	TRAY TYPE	MIN DIAMETER MM
1	2 - 12	N/A	609.60	1.00	VALVE	381.00

UNIT 6, 'WATER_REC'

TOTAL NUMBER OF ITERATIONS

SURE METHOD 51

COLUMN SUMMARY

TRAY	TEMP DEG C	PRESSURE KPA		---------- NET FLOW RATES ---------- LIQUID KG-MOL/HR	VAPOR	FEED	PRODUCT	HEATER DUTIES M*KJ/HR
1	59.9	20.00	131.8		127.1L	260.0V		
2	60.3	20.35	131.8	264.7				
3	60.7	20.70	130.6	264.8				
4	67.1	21.05	317.1	263.6	211.2L			
5	142.7	21.40	265.7	238.9				
6R	206.2	21.75		187.5		78.2L	15.8999	

TRAY SIZING MECHANICAL DATA

SECTION	TRAY NUMBERS	TRAY PASSES	TRAY SPACING MM	SYSTEM FACTOR	TRAY TYPE	MIN DIAMETER MM
1	1 - 5	N/A	609.60	1.00	VALVE	381.00

UNIT 9, 'TEG_REC'

TOTAL NUMBER OF ITERATIONS

SURE METHOD 17

COLUMN SUMMARY

TRAY	TEMP DEG C	PRESSURE KPA	---------- NET FLOW RATES ---------- LIQUID KG-MOL/HR	VAPOR	FEED	PRODUCT	HEATER DUTIES M*KJ/HR
1C	79.6	2.00	88.4			16.0L	-6.0115
2	96.0	2.00	78.0	104.4			
3	133.8	3.00	64.5	94.0			
4	164.0	4.00	122.1	80.5	78.2M		
5	178.0	5.00	123.6	59.8			
6	187.7	6.00	125.3	61.3			
7R	194.3	7.00	63.0		62.2L	5.2327	

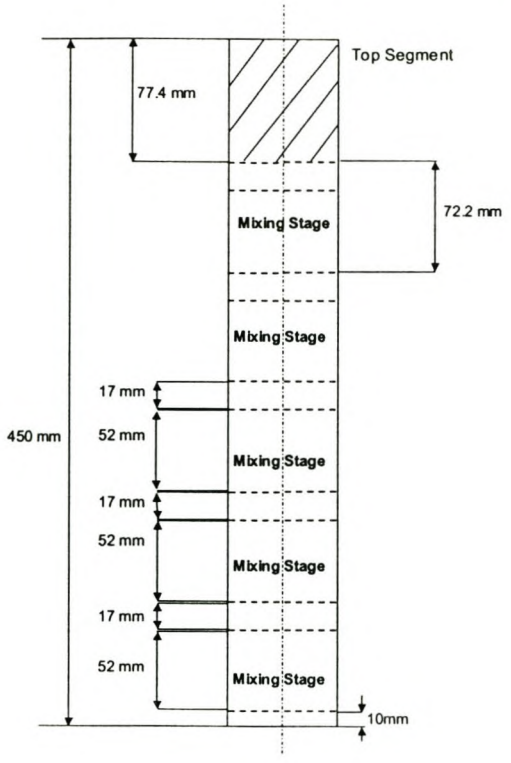
PACKED COLUMN DATA

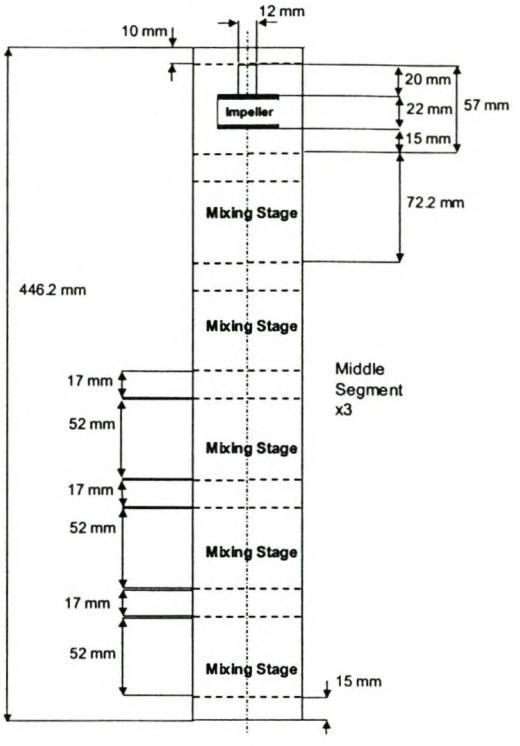
SECTION 1 PACKED HEIGHT = 3.00 M
HETP = 0.600 M
COLUMN ID = 1.880 M
PACKING TYPE (SULZER-98) = M250.X
MAXIMUM % CAPACITY = 50.00
F-FACTOR = 1.80 PA ** 0.5
F-FACTOR (3 mbar/m) = 3.92 PA ** 0.5
% CAPACITY (3 mbar/m) = 71.30

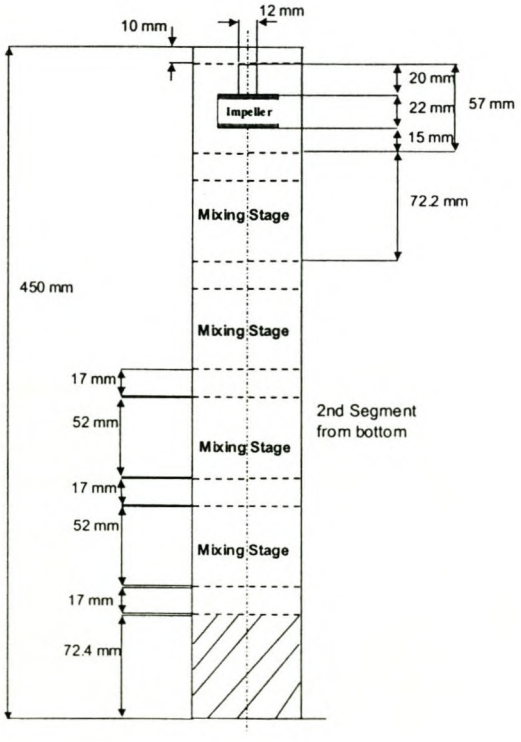
STREAM DATA IS GIVEN IN CHAPTER 8, TABLE 8-1

APPENDIX E: CONSTRUCTION OF PILOT PLANT EXTRACTION COLUMN

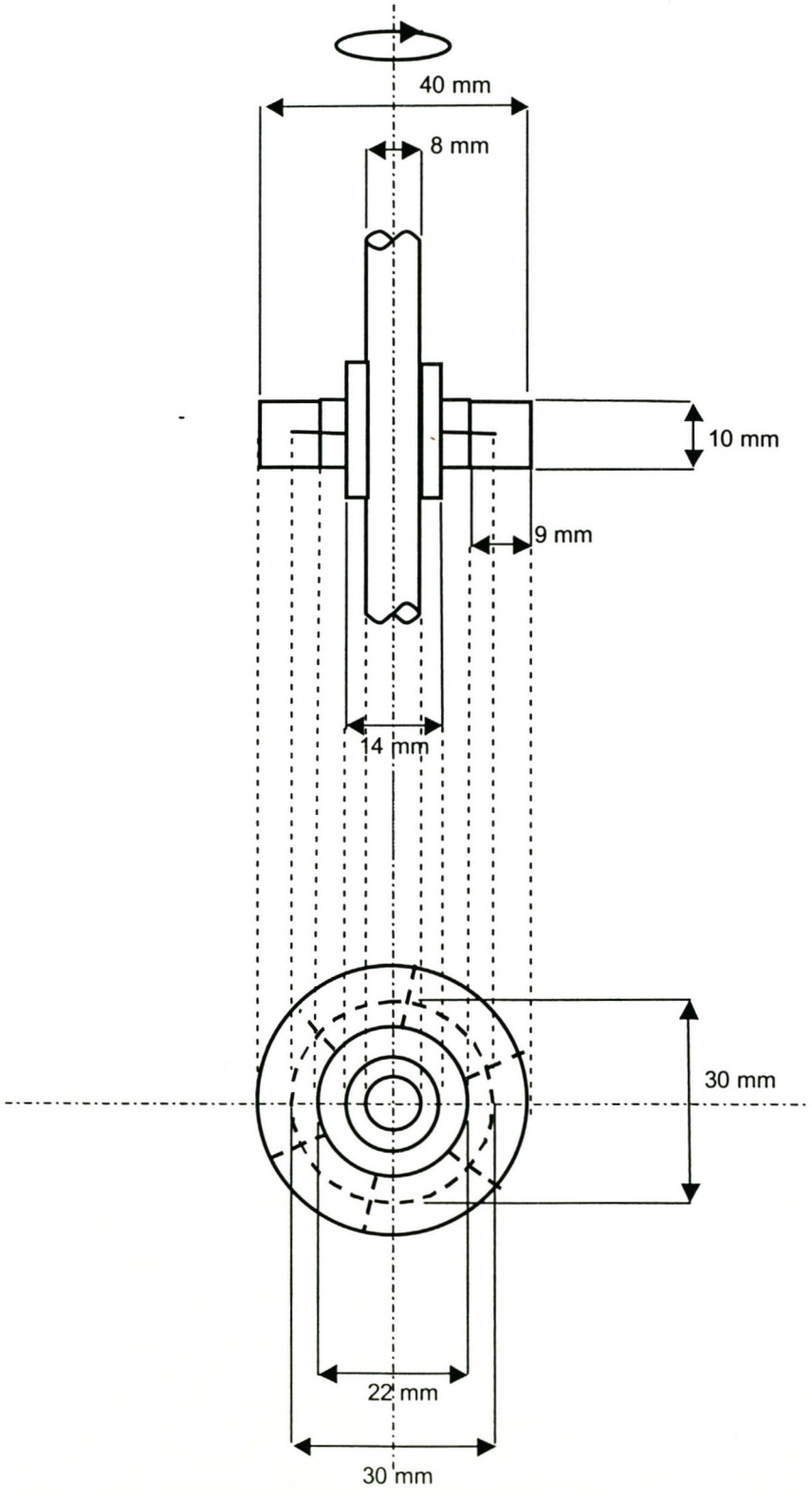
E1: Distribution of Mixing Stages Through Column



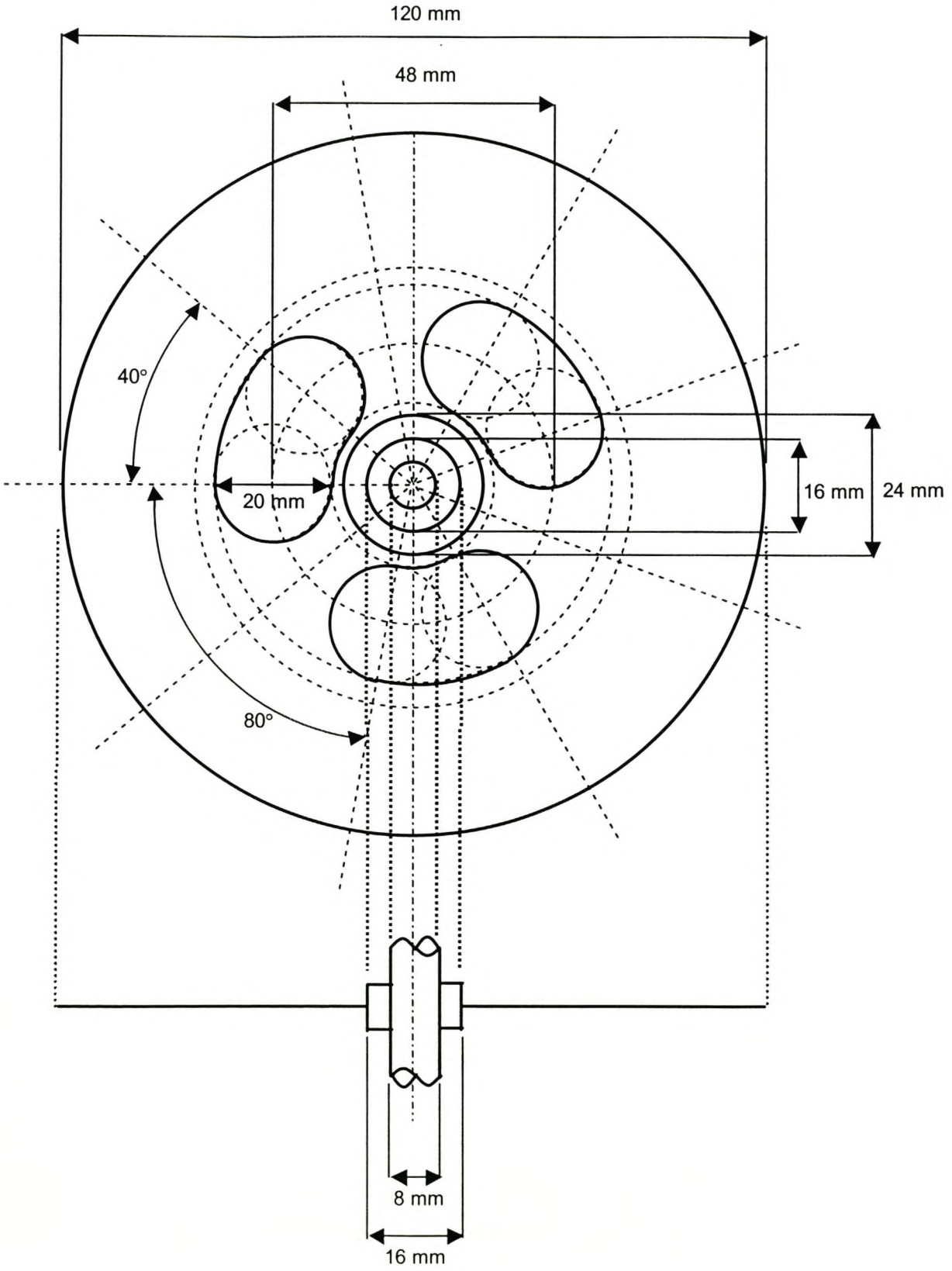




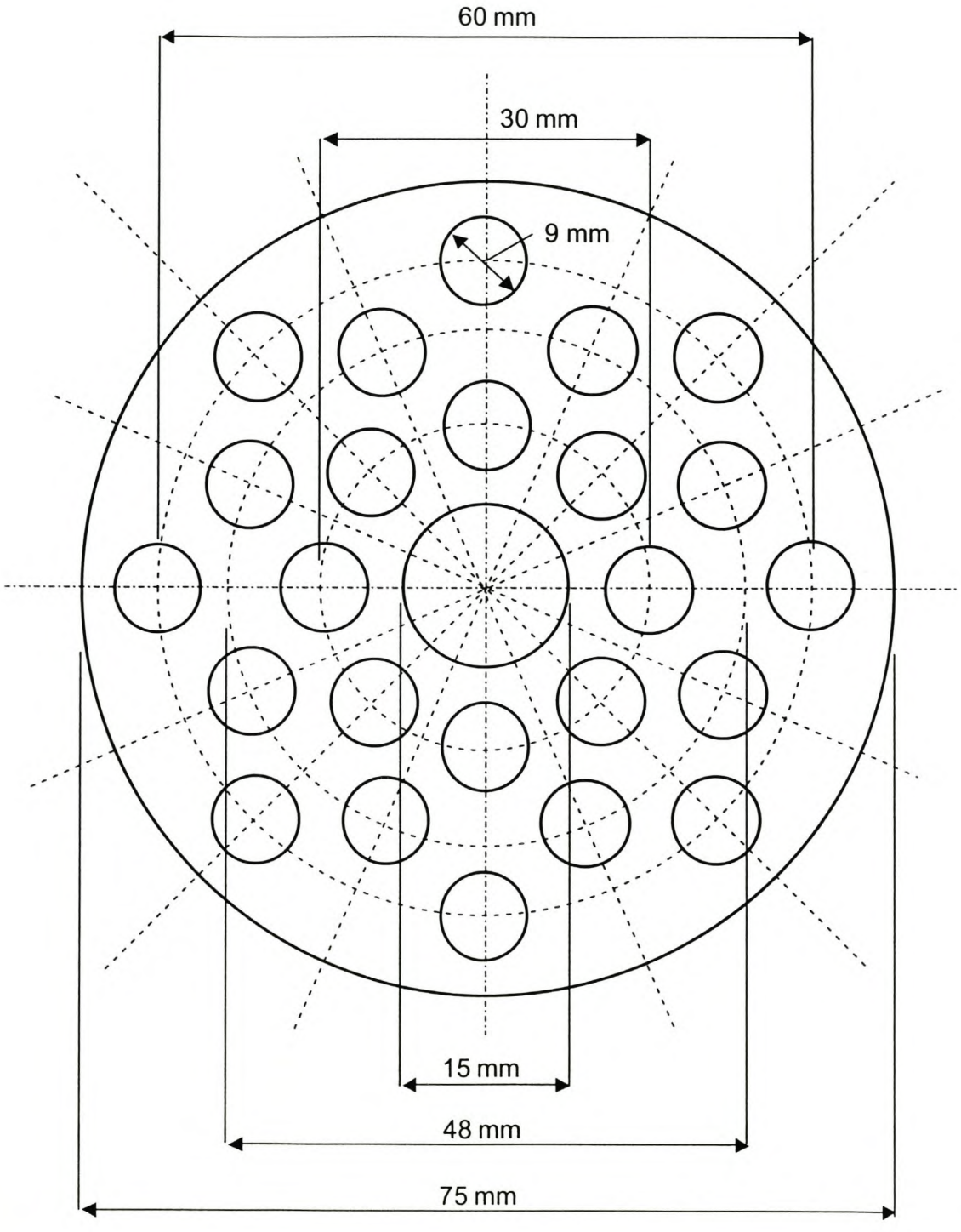
E2. Diagram of Impeller



E3: Diagram of Bearing Plate



E4: Diagram of Stator Plate



APPENDIX F: PILOT PLANT CALCULATIONS

F1: Pilot Plant test on Industrial Feed Stream

WCA = Wet Chemical Analysis; GC = Gas Chroamtography

First Pass through Extractor

Composition of Feed Stream

Sample Mass : 171.2 g
Mass of Phenolics in Feed (WCA) : 81.7 g
Mass of Neutral Oils and Nitrogen Bases: 82.1g
(combined water soluble and insoluble masses less mass determined with GC in water soluble fraction) :
Error on Sample Mass Balance = (82.1+81.7 - 171.2)/171.2 x 100 = -4.3%

Composition of Solvent Stream

19.9% water
80.1% TEG

Process Stream Flowrates [kg/h]:

- Feed (measured) = 4.6
- Water + TEG (measured) = 17.2
- Hexane (measured) = 22.0
- Extract (measured) = 19.55
- Raffinate (mass balance over column) = 24.25

Table F1-1: Composition of Extract After First Pass Through Column (GC analysis + Karl Fischer Titration):

Component	Mass Percentage Concentration
Hexane	0.2
Water	18.3
TEG	70.2
Neutral Oils and Nitrogen Bases	0.24
Phenolic Compounds	11.08

I.e. Phenolic Flowrate in Extract = 0.1108*19.55=2.166 [kg/h]
Phenolic Recovery = 2.170 / 2.29 = 94.59%

Phenolic Purity with respect to neutral oils and nitrogen bases
= 11.08/(11.08+0.24)
=97.89 %

Composition of Raffinate After First Pass Through Column :

Mass of Sample: 64.1g
Mass hexane distilled off :57.3g
Mass water (Karl Fischer) : 0.02g
Mass TEG (GC analysis) : 0.00g
Mass of Neutral Oils and Nitrogen Bases (WCA + GC analysis) : 6.3 g
Mass of Phenolic Compounds (WCA + GC analysis) : 0.476 g

Table F1-2: Composition of Raffinate After First Pass Through Column (GC analysis + Karl Fischer Titration + WCA):

Component	Mass Percentage Concentration
Hexane	89.4
Water	0.03
TEG	0.00
Neutral Oils and Nitrogen Bases	9.9
Phenolic Compounds	0.7

Table F1-3: Mass Balance Over Column for First Extraction

FLOW RATES [kg/h]	IN	Extract	Raffinate	Error
hexane	22	**0.044**	21.67	**-1.3**
water	3.43	**3.578**	0.01	**4.6**
TEG	13.77	**13.715**	0.00	**-0.4**
Neural Oils and Nitrogen Bases	2.31	**0.047**	2.39	**5.8**
Phenolics	2.29	**2.167**	0.18	**2.3**

Second Pass Through Extractor

Process Stream Flowrates [kg/h]:

- Feed + Solvent (measured) = 22.3
- Hexane (measured) = 22.0
- Extract (measured) = 22.1
- Raffinate (mass balance over column) = 22.3

Table F1-4: Composition of Extract After First Pass Through Column (GC analysis + Karl Fischer Titration):

Component	Mass Percentage Concentration
Hexane	0.2
Water	19.1
TEG	69.7
Neutral Oils and Nitrogen Bases	0.21
Phenolic Compounds	10.86

Phenolic Recovery = 0.1086x22.1 / 0.1108 x 22.3 = 96.91%
Phenolic Purity with respect to neutral oils and nitrogen bases: 98.09 %

Composition of Raffinate After First Pass Through Column :

Mass of Sample: 696.3g
Mass hexane distilled off :683.96g
Mass water (Karl Fischer) : 0.00g
Mass TEG (GC analysis) : 0.00g
Mass of Neutral Oils and Nitrogen Bases (WCA + GC analysis) : 0.934 g
Mass of Phenolic Compounds (WCA + GC analysis) : 0.966 g

Table F1-5: Composition of Raffinate After First Pass Through Column (GC analysis + Karl Fischer Titration + WCA):

Component	Mass Percentage Concentration
Hexane	99.64
Water	0.0
TEG	0.0
Neutral Oils and Nitrogen Bases	0.18
Phenolic Compounds	0.18

Table F1-6: Mass Balance Over Column for 2nd Extraction

FLOW RATES [kg/h]	Feed	Extract	Raffinate	Error
Hexane	22.04	0.037	22.19	0.8
Water	4.08	4.212	0.0	3.2
TEG	15.64	15.359	0.000	-1.8
Neutral Oils and Nitrogen Bases	0.05	0.047	0.02	21.0
Phenolics	2.47	2.395	0.04	-1.3

Water Recovery column

Table F1-4: Percentage Composition of Feed, Distillate and Bottoms of Water Recovery Column:

Components	Feed	Distillate	Bottoms
Hexane	0.2	**1.1**	0.0
water	19.1	**97.8**	1.7
TEG	69.6	**0.0**	85.0
Neutral Oils and Nitrogen Bases	0.2	**1.0**	0.03
Phenolics	10.9	**0.2**	13.27

Percentage purity Phenolics with respect to neutral oils and nitrogen bases: 99.77%

A portion of the distillate was removed through the vacuum system.

Mass of bottoms / Mass feed = 0.819

Percentage Phenolic recovery = 0.1327 x 81.9 / 0.109 x 100 =99.7%

APPENDIX G: PUBLICATIONS PROCEEDING FROM STUDY

Venter D.L., Nieuwoudt I. "Liquid-Liquid Equilibria for m-Cresol + o-Toluonitrile + Hexane + Water + (Glycerol or Triethylene Glycol) at 313.15 K", Journal of Chemical and Engineering Data, *1998, 43(4), 676-680.*

Venter D.L., Nieuwoudt I. "The separation of m-cresol from neutral oils with liquid-liquid extraction", *Industrial and Engineering Chemistry Research,* 1998, 37(10), 4099-4106.

Papers submitted

Venter D.L., Nieuwoudt I. "Liquid-liquid equilibria for the separation of phenolic compounds and neutral oils", Journal of Chemical and Engineering Data, *Submitted for publication.*

International Conferences

Nieuwoudt I., Venter D.L. "The separation of phenolic compounds and neutral oils", International Solvents Extraction Conference, Barcelona, Spain, July 1999, Award winning contribution.

Venter D.L., Nieuwoudt I. "The separation of phenolic compounds and neutral oils" Achema 2000, Frankfurt, Germany, May 2000.

Patents

Nieuwoudt, I. and Venter, D.L. "Separation of phenolic compounds and neutral oils" Priority Date 9 October 1997, South African Patent Office. Patent number: ZA9811312.

APPENDIX H: NOMENCLATURE

Symbol	Description	Dimension
A	matrix of first derivatives of the objective function with respect to adjustable parameters	-
$\Delta\mathbf{A}^*$	parameter difference matrix	-
b_{ij}	NRTL binary parameter for component i and j interaction	-
E	mass flowrate of extract stream	[kg/h]
F	goal function to be minimised (Chapter 6)	-
F	mass flowrate of feed stream (Chapter 7)	[kg/h]
G_{ij}	NRTL empirical parameter	-
H	mass flowrate of hexane stream (Chapter 7)	[kg/h]
i	integer	-
I	identity matrix	-
k	integer	-
K	distribution coefficient	-
m_l	median (Chapter 6)	-
m	mass	[kg]
$\mathbf{N_T}$	number of theoretical stages	-
n	integer	-
P	component purity	[%]
R	mass flowrate of raffinate stream	[kg/h]
R,	Percentage recovery of component	[%]
T	temperature	[K]
V^k:	velocity of particle at time-steps k	$[s^{-1}]$
w	weight for goal function term	-
W_o	inertia of a particle in a particle swarm algorithm	-
x	equilibrium fraction of component in liquid phase	-
Y	specified output parameter	-
Y*	predicted output parameter	-
α_{ij}	NRTL empirical parameter	-
β_{ij}	separation factor of component i relative to j	-
δ	absolute difference	-
ε	error term in goal function (Chapter 6)	-
ε	percentage error	-
γ	activity coefficient	-
σ	standard deviation	-
η	stage efficiency	[%]
ω	impeller rotation speed	rpm

Symbol	Description	Dimension
	Subscript	
A	solute A	-
B	solute B	-
i	component i	-
j	component j	-
	Superscript	
F	Feed stream	-
H	Hexane stream	-
I	Extract phase	-
II	Raffinate phase	-
	Abbreviations	
S/F	Solvent to feed mass ratio	-
H/F	Hexane to feed mass ratio	-
W/S	Water to solvent mass ratio	